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Review

The chemical diversity and distribution of glucosinolates and isothiocyanates among plants☆

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Abstract

Glucosinolates (β-thioglucoside-*N*-hydroxysulfates), the precursors of isothiocyanates, are present in sixteen families of dicotyledonous angiosperms including a large number of edible species. At least 120 different glucosinolates have been identified in these plants, although closely related taxonomic groups typically contain only a small number of such compounds. Glucosinolates and/or their breakdown products have long been known for their fungicidal, bacteriocidal, nematocidal and allelopathic properties and have recently attracted intense research interest because of their cancer chemoprotective attributes. Numerous reviews have addressed the occurrence of glucosinolates in vegetables, primarily the family Brassicaceae (syn. Cruciferae; including *Brassica* spp and *Raphanus* spp). The major focus of much previous research has been on the negative aspects of these compounds because of the prevalence of certain "antinutritional" or goitrogenic glucosinolates in the protein-rich defatted meal from widely grown oilseed crops and in some domesticated vegetable crops. There is, however, an opposite and positive side of this picture represented by the therapeutic and prophylactic properties of other "nutritional" or "functional" glucosinolates. This review addresses the complex array of these biologically active and chemically diverse compounds many of which have been identified during the past three decades in other families. In addition to the *Brassica* vegetables, these glucosinolates have been found in hundreds of species, many of which are edible or could provide substantial quantities of glucosinolates for isolation, for biological evaluation, and potential application as chemoprotective or other dietary or pharmacological agents.

Keywords: Cancer; Chemoprotection; Edible plants; Functional food; Myrosinase; Crucifers

Contents

☆ This paper is dedicated to Professor Anders Kjær, who, with his collaborators in Lyngby, Denmark, has contributed immeasurably to the scientific community's understanding of glucosinolates and to knowledge of their chemistry, biosynthesis, metabolism, and their relationship to the plants from which they were isolated; more glucosinolates have been isolated and characterized in Professor Kjær's laboratory than anywhere else in the world.

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1. Introduction

The first observations on the unique properties of glucosinolates and isothiocyanates or mustard oils, as they are commonly known, were recorded at the beginning of the 17th century as a result of efforts to understand the chemical origin of the sharp taste of mustard seeds. The discovery and early history of glucosinolates and the participation of the enzyme myrosinase (a β-thioglucosidase) in their conversion to isothiocyanates, are the subjects of an interesting and scholarly review by Challenger (1959). The glucosinolates known by the trivial names sinigrin (2-propenyl or allyl glucosinolate; **107**) and sinalbin (4-hydroxybenzyl glucosinolate; **23**) were isolated early in the 1830s from black (*Brassica nigra*) and white (*Sinapis alba*) mustard seeds, respectively.[2] (See Tables 1 and 2 for glucosinolate numbers used throughout this review.) The first general, although incorrect, structure for these compounds was proposed at the end of the nineteenth century by Gadamer (1897), who concluded that the side chain was linked to the nitrogen rather than the carbon atom of the "NCS" group. Despite certain difficulties the structure was generally assumed to be correct until 1956, when Ettlinger and Lundeen (1956a) pointed out the inadequacies of the Gadamer structure to explain certain properties of these compounds, proposed the now correct structure, and described the first chemical synthesis of a glucosinolate (Ettlinger and Lundeen, 1957). The remaining structural issue of the geometrical isomerism at the C=N bond was established to be *Z* (or anti-) by X-ray crystallographic analysis of sinigrin (see Fig. 1; Marsh and Waser, 1970).

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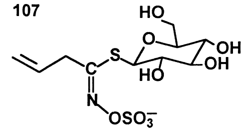

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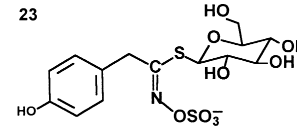


Glucosinolates are β-thioglucoside *N*-hydroxysulfates [also known as (*Z*)-(or *cis*)-*N*-hydroximinosulfate esters or *S*-glucopyranosyl thiohydroximates], with a side chain (R) and a sulfur-linked β-D-glucopyranose moiety.

In the last 40 years, a succession of reviews have addressed the biology and chemistry of glucosinolates (e.g. Kjær, 1961, 1974; Ettlinger and Kjær, 1968; Kjær and Olesen Larsen, 1973, 1976; Underhill et al., 1973;

[2] Glucosinolates are arranged alphabetically by chemical name and assigned unique sequential identifying bold numbers in Table 1 which also provides the common (trivial) names. These numbers are used throughout this paper. Glucosinolates are listed alphabetically by common name in Table 2. Note that not all glucosinolates have been assigned common names. Chemical structures are shown in Fig. 1 in which the compounds are grouped by structural classes. Since the stereochemistry of sulfinyl groups and at carbon centers has not been established for many glucosinolates, the isomeric nature of the compounds is not specified. In Appendix A glucosinolates are referred to by bold number only. The chemical and common names provided by the original authors have not been altered to reflect current IUPAC systematic names, since this would make it too confusing for those interested in checking the original references.

Table 1
Chemical and common names of glucosinolates identified in higher plants. Numerical designations are used in the review. Class assignments refer to structure-based assignment of glucosinolates to chemical classes (see Fig. 1)

		Glucosinolate	
No.	Class	Chemical name	Common names
1	F	3-Methoxycarbonylpropyl	Glucoerypestrin
2	I	1-Acetyl-indol-3-ylmethyl	1-Acetyl-glucobrassicin
3	J	4-(4′-*O*-Acetyl-α-L-rhamnopyranosyloxy)benzyl	
4	J	2-(α-L-Arabinopyranosyloxy)-2-phenylethyl	
5	H	4-(Benzoyloxy)butyl	
6	H	2-(Benzoyloxy)ethyl	
7	H	2-Benzoyloxy-1-ethylethyl	Glucobenzsisaustricin
8	H	Benzoyloxymethyl	
9	H	2-Benzoyloxy-1-methylethyl	Glucobenzosisymbrin
10	H	3-(Benzoyloxy)propyl	Glucomalcomiin
11	G	Benzyl	Glucotropaeolin
12	D	3-Butenyl	Gluconapin
13	B	*n*-Butyl	
14	G	3,4-Dihydroxybenzyl	Glucomatronalin
15	G	3,4-Dimethoxybenzyl	
16	B	Ethyl	Glucolepidiin
17	E	1-Ethyl-2-hydroxyethyl	Glucosisaustricin
18	D	6-Heptenyl	
19	D	5-Hexenyl	
20	B	*n*-Hexyl	
21	G	2-Hydroxybenzyl	
22	G	3-Hydroxybenzyl	Glucolepigramin
23	G	4-Hydroxybenzyl	[Gluco]sinalbin
24a	D	2(*R*)-2-Hydroxy-3-butenyl	Progoitrin
24b	D	2(*S*)-2-Hydroxy-3-butenyl	Epiprogoitrin
25	E	3-Hydroxybutyl	
26	E	4-Hydroxybutyl	
27	E	2-Hydroxyethyl	
28	I	4-Hydroxyindol-3-ylmethyl	4-Hydroxyglucobrassicin
29	E	2-Hydroxy-2-methylbutyl	Glucocleomin
30	E	1-(Hydroxymethyl)propyl	
31	E	2-Hydroxy-2-methylpropyl	Glucoconringiin
32	A	3-Hydroxy-6-(methylsulfinyl)hexyl	
33	A	3-Hydroxy-5-(methylsulfinyl)pentyl	
34	A	3-Hydroxy-6-(methylsulfonyl)hexyl	
35	A	3-Hydroxy-5-(methylsulfonyl)pentyl	
36	A	3-Hydroxy-6-(methylthio)hexyl	
37	A	3-Hydroxy-5-(methylthio)pentyl	
38	D	2-Hydroxy-4-pentenyl	[Gluco]napoleiferin
39	E	2-Hydroxypentyl	
40	G	2(*R*)-Hydroxy-2-phenylethyl	Glucobarbarin
41	E	2-Hydroxypropyl	
42	E	3-Hydroxypropyl	
43	I	Indol-3-ylmethyl	Glucobrassicin
44	G	2-Methoxybenzyl	
45	G	3-Methoxybenzyl	Glucolimnanthin
46	G	4-Methoxybenzyl	Glucoaubrietin
47	I	1-Methoxyindol-3-ylmethyl	Neoglucobrassicin
48	I	4-Methoxyindol-3-ylmethyl	4-Methoxyglucobrassicin
49	G	2-(4-Methoxyphenyl)-2,2-dimethylethyl [or 2,2-dimethyl-2-(4-methoxyphenyl)ethyl]	
50	G	2-(4-Methoxyphenyl)-2-hydroxyethyl [or 2-hydroxy-2-(4-methoxyphenylethyl)]	
51	B	Methyl	Glucocapparin
52	D	3-Methyl-3-butenyl	
53	C	1-Methylbutyl	
54	C	2-Methylbutyl	
55	C	3-Methylbutyl	
56	C	1-Methylethyl	Glucoputranjivin, isopropyl
57	E	1-Methyl-2-hydroxyethyl	Glucosisymbrin
58	C	3-Methylpentyl	
59	C	4-Methylpentyl	

(*continued on next page*)

Table 1 (*continued*)

No.	Class	Glucosinolate: Chemical name	Common names
60	D	2-Methyl-2-propenyl	
61	C	1-Methylpropyl	Glucocochlearin, glucojiabutin, sec-Butyl, 2-Butyl
62	C	2-Methylpropyl	Isobutyl
63	A	4-Methylsulfinyl-3-butenyl	Glucoraphenin
64	A	4-(Methylsulfinyl)butyl	Glucoraphanin
65	A	10-(Methylsulfinyl)decyl	Glucocamelinin
66	A	7-(Methylsulfinyl)heptyl	Glucoibarin
67	A	6-(Methylsulfinyl)hexyl	Glucohesperin
68	A	9-(Methylsulfinyl)nonyl	Glucoarabin
69	A	8-(Methylsulfinyl)octyl	Glucohirsutin
70	A	7-Methylsulfinyl-3-oxoheptyl	
71	A	8-Methylsulfinyl-3-oxooctyl	
72	A	5-(Methylsulfinyl)pentyl	Glucoalyssin
73	A	3-(Methylsulfinyl)propyl	Glucoiberin
74	A	11-(Methylsulfinyl)undecyl	
75	A	4-Methylsulfonyl-3-butenyl	
76	A	4-(Methylsulfonyl)butyl	Glucoerysolin
77	A	10-(Methylsulfonyl)decyl	
78	A	6-(Methylsulfonyl)hexyl	
79	A	9-(Methylsulfonyl)nonyl	
80	A	8-(Methylsulfonyl)octyl	
81	A	5-(Methylsulfonyl)pentyl	
82	A	3-(Methylsulfonyl)propyl	Glucocheirolin
83	A	4-Methylthio-3-butenyl	Dehydroerucin
84	A	4-(Methylthio)butyl	Glucoerucin
85	A	10-(Methylthio)decyl	
86	A	2-(Methylthio)ethyl	Glucoviorylin
87	A	7-(Methylthio)heptyl	
88	A	6-(Methylthio)hexyl	Glucolesquerellin
89	A	9-(Methylthio)nonyl	
90	A	7-Methylthio-3-oxoheptyl	
91	A	6-Methylthio-3-oxohexyl	
92	A	8-(Methylthio)octyl	
93	A	8-Methylthio-3-oxooctyl	
94	A	5-(Methylthio)pentyl	Glucoberteroin
95	A	3-(Methylthio)propyl	Glucoiberverin
96	F	4-Oxoheptyl	Glucocapangulin; glucopangulin
97	F	5-Oxoheptyl	Gluconorcappasalin
98	F	5-Oxooctyl	Glucocappasalin
99	F	4-Oxopentyl or 3-(Methylcarbonyl)propyl	
100	D	1-Pentenyl	
101	D	4-Pentenyl	Glucobrassicanapin
102	B	*n*-Pentyl	
103	G	Phenyl	
104	G	4-Phenylbutyl	
105	G	2-Phenylethyl	Gluconasturtiin; phenethyl
106	G	3-Phenylpropyl	
107	D	2-Propenyl	Allyl, Sinigrin
108	B	*n*-Propyl	
109	J	2-(α-L-Rhamnopyranosyloxy)benzyl	
110	J	4-(α-L-Rhamnopyranosyloxy)benzyl	
111	J	6-Sinapoyl-β-D-1-thioglucoside of 4-methylsulfinylbut-3-enyl	
112	I	1-Sulfo-indol-3-ylmethyl	Glucobrassicin-1-sulfate
113	E	4,5,6,7-Tetrahydroxydecyl	
114	G	3,4,5-Trimethoxybenzyl	
115[a]		"*iso*"-Heptyl	
116[a]		"*iso*"-Hexyl	
117[b]	H	5-(Benzoyloxy)pentyl	
118[b]	H	6-(Benzoyloxy)hexyl	
119[c]		3-*O*-Apiosylglucomatronalin	
120[c]		3-*O*-Apiosylglucomatronalin 3,4-dimethoxybenzoyl ester	

[a] Structures unresolved; Grob and Matile (1980).
[b] Added in proof; Haughn et al. (1991); identified in *Arabidopsis* sp.
[c] Larsen et al. (1992); however, the identification of these compounds references only unpublished work.

Table 2
Alphabetical listing of common names of glucosinolates identified in higher plants[a]

Common name	Number	Chemical class	Common name	Number	Chemical class
1-Acetylglucobrassicin	**2**	I	Glucoiberverin	**95**	A
Dehydroerucin	**83**	A	Glucojiabutin	**61**	C
Epiprogoitrin	**24b**	D	Glucolepidiin	**16**	B
Glucoalyssin	**72**	A	Glucolepigramin	**21**	G
Glucoarabin	**68**	A	Glucolesquerellin	**88**	A
Glucoaubrietin	**46**	G	Glucolimnanthin	**45**	G
Glucobarbarin	**40**	G	Glucomalcomiin	**10**	H
Glucobenzosisymbrin	**9**	H	Glucomatronalin	**14**	G
Glucobenzsisaustricin	**7**	H	Gluconapin	**12**	D
Glucoberteroin	**94**	A	Gluconapoleiferin	**38**	D
Glucobrassicanapin	**101**	D	Gluconasturtiin	**105**	G
Glucobrassicin	**43**	I	Gluconorcappasalin	**97**	F
Glucobrassicin-1-sulfate	**112**	I	Glucoputranjivin	**56**	C
Glucocamelinin	**65**	A	Glucoraphanin	**64**	A
Glucocapangulin; glucopangulin	**96**	F	Glucoraphenin	**63**	A
Glucocapparin[b]	**51**	B	Glucosinalbin	**23**	G
Glucocappasalin	**98**	F	Glucosisaustricin	**17**	E
Glucocheirolin	**82**	A	Glucosisymbrin	**57**	E
Glucocleomin	**29**	E	Glucotropaeolin	**11**	G
Glucocochlearin	**61**	C	Glucoviorylin	**86**	A
Glucoconringiin	**31**	E	4-Hydroxyglucobrassicin	**28**	I
Glucoerucin	**84**	A	4-Methoxyglucobrassicin	**48**	I
Glucoerypestrin	**1**	F	Napoleiferin	**38**	D
Glucoerysolin	**76**	A	Neoglucobrassicin	**47**	I
Glucohesperin	**67**	A	Progoitrin	**24a**	D
Glucohirsutin	**69**	A	Sinalbin	**23**	G
Glucoibarin	**66**	A	Sinigrin	**107**	D
Glucoiberin	**73**	A			

[a] Note that not all isolated glucosinolates have been assigned common names.
[b] Also designated glucoapparin by Benn (1964b).

Underhill, 1980; Fenwick et al., 1983; Chew, 1988; Duncan and Milne, 1989; Brown and Morra, 1997; Halkier, 1999; Mithen et al., 2000), and their distribution among plants (Rodman, 1981). More narrowly focused reviews have examined the indole glucosinolates (McDanell et al., 1988), or specifically glucosinolates in the family Brassicaceae (Kjær, 1976). Similar coverage (i.e. of glucosinolates of crop plants, primarily the *Brassica* vegetables) has been provided by Stoewsand (1995) and Rosa et al. (1997). Many other even more narrowly focused reviews have concentrated on specific plant families or on specific aspects of glucosinolate biology and they are referenced herein, as appropriate.

The present review provides a comprehensive survey of the chemical structures of all known glucosinolates and the plant families from which they have been isolated. It provides a single source of their chemical structure, their trivial names, and groups these compounds into families according to their structural similarities. We discuss, mostly by reference, the state of scientific understanding of the synthesis, biosynthesis and ecological importance of glucosinolates and their conversion to isothiocyanates and other products by myrosinase. To our knowledge, there has been no recent effort to provide a comprehensive compilation and cataloging of isolated glucosinolates, their structures, systematic and trivial (common) names, and their distribution among plant species. Although we have attempted to do so herein, undoubtedly there are omissions. Since many of these compounds were identified before modern spectroscopic techniques were available, some of the structural assignments of glucosinolates to plant taxa may require revision.

2. Glucosinolate distribution among plants

There is now a voluminous literature on the glucosinolates of the plant family, Brassicaceae, which alone contains more than 350 genera and 3000 species. Of the many hundreds of cruciferous species investigated, all are able to synthesize glucosinolates (Kjær, 1976). Among the Brassicaceae, the genus *Brassica* contains a large number of the commonly consumed species. *Brassica* sp. glucosinolates have been the subject of scholarly reviews by Kjær (1974, 1976), Fenwick et al. (1983), Chew (1988), McDanell et al. (1988), Duncan and Milne (1989), Stoewsand (1995) and most recently by Rosa et al. (1997). Glucosinolates are by no means confined to

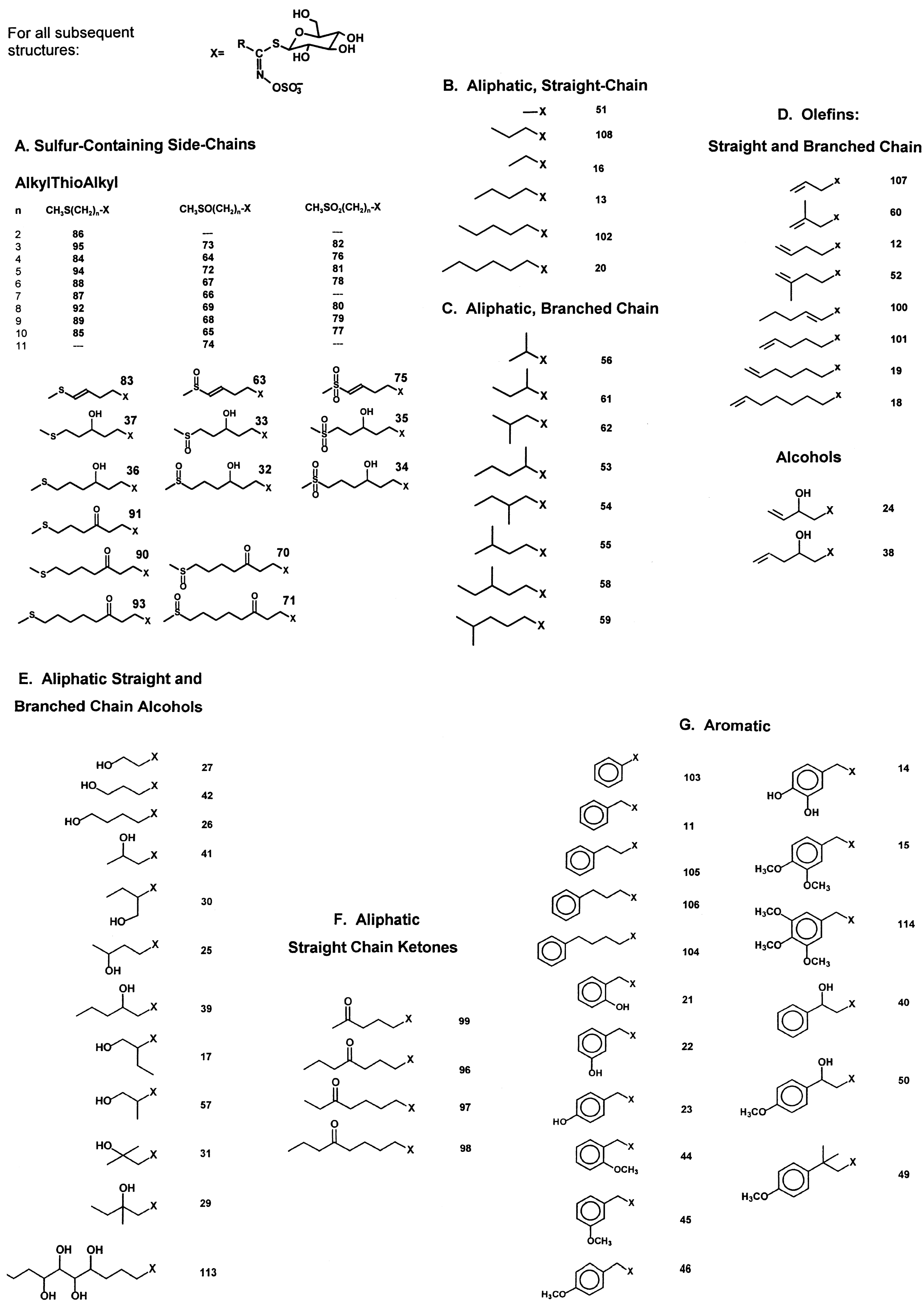


Fig. 1. Classification of glucosinolates according to chemical structures. [a] Elliott and Stowe (1970) have isolated the sulfate derivative of glucobrassicin (**112**) from *Isatis tinctoria* and Schraudolf and Bauerle (1986) have isolated the acetyl derivative (**2**) from *Tovaria pendula*, but structural assignment should be regarded as tentative (McDanell et al., 1988) (*continued on next page*).

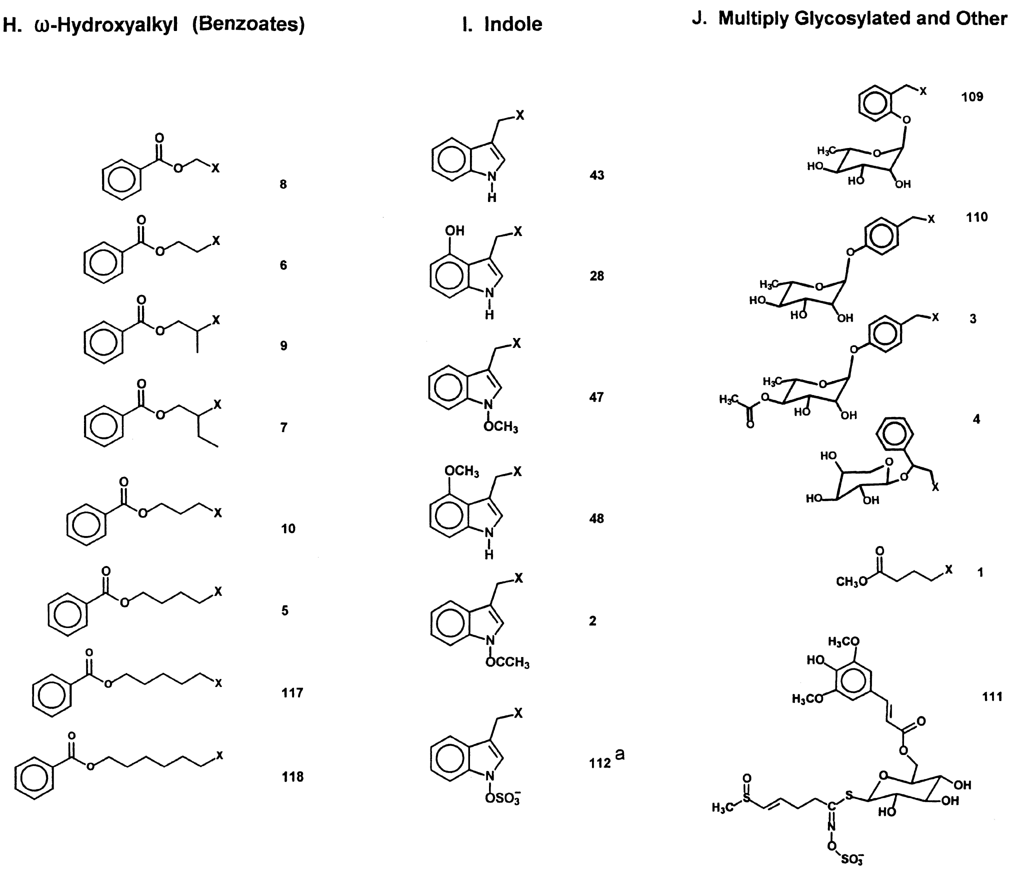


Fig. 1 (*continued*).

crucifers; at least 500 species of non-cruciferous dicotyledonous angiosperms have been reported to contain one or more of the over 120 known glucosinolates (Table 1). Most glucosinolate-containing genera are clustered within the Brassicaceae, Capparaceae and Caricaceae; of the sixteen families listed in Table 3, these include the largest number of glucosinolate-containing species (Rodman, 1981). Indeed, the capacity to biosynthesize glucosinolates has been used as a taxonomic marker to support evolution-based classification schemes (Rodman, 1981, 1991a,b; Mithen et al., 1987a; Rodman et al., 1993). Methyl glucosinolate, for example, is not found in the Brassicaceae, but is a distinctive component of the closely related Capparaceae. Glucosinolates with glycosylated R-groups appear limited to the Resedaceae and Moringaceae. Although the idea that there are taxon-specific glucosinolates is intriguing, this view is not highly developed and it is beyond the scope of this review. Rodman (1981) maintained that by the early 1980s, the taxonomic distribution of glucosinolates was fairly well known and that surprising discoveries of additional glucosinolate-containing plants would be likely to come from less-well-studied tropical plant families. For example the Euphorbiaceae, a vast family found primarily in the warmer parts of the world, was then and still is the only glucosinolate-containing family in which all genera except one (*Drypetes*; syn. *Putranjiva*) explicitly lack the capacity to produce glucosinolates and myrosinase. However, these compounds have only been searched for in a very small number of the estimated 5000 or more species within this family.

3. Glucosinolate chemistry

3.1. Types of glucosinolates

We have grouped glucosinolates into a number of chemical classes on the basis of structural similarities. The most extensively studied glucosinolates are the aliphatic, ω-methylthioalkyl, aromatic and heterocyclic (e.g. indole) glucosinolates, typified by those found in the *Brassica* vegetables (e.g. compounds **12, 23, 24, 38, 43, 47, 56, 61, 63, 64, 72, 73, 84, 94, 95, 100, 101, 105, 107** in Table 1 and Fig. 1). Glucosinolate side chains, however, are characterized by a wide variety of chemical structures (Fig. 1). The most numerous glucosinolates are those containing either straight or branched carbon chains. Many of these compounds also contain double bonds (olefins), hydroxyl or carbonyl groups, or sulfur

Table 3
Sixteen families of glucosinolate-containing angiosperms[a]

Family	Chemical class	Glucosinolates
Bataceae	I	**28, 43**
Brassicaceae	A–J	**1, 5–20, 22–26, 28–48, 50, 51, 53–69, 72–84, 86–89, 91–95, 99–107, 111, 112, 114**
Bretschneideraceae	E, G	**14, 31**
Capparaceae	A, B, C, D, E, F, G, I	**12, 13, 23, 24, 28, 29, 43, 47, 48, 51, 52, 54, 56, 73, 96–98, 107, 108**
Caricaceae	G	**11**
Euphorbiaceae	C, E	**26, 29, 56**
Gyrostemonaceae	C	**61, 62**
Limnanthaceae	E, G	**31, 45**
Moringaceae	C, E, G, J	**3, 11, 23, 31, 56, 61, 62, 110**
Pentadiplandraceae	G	**11, 49**
Phytolaccaceae	C, E, G	**11, 22, 23, 29, 61**
Pittosporaceae	G	**23**
Resedaceae	E, G, I, J	**4, 11, 21–23, 31, 40, 43, 47, 105, 109**
Salvadoraceae	C, G	**11, 23, 56**
Tovariaceae	C	**2, 11, 43, 47, 56**
Tropaeolaceae	B, C, E, G	**11, 16, 23, 31, 46, 56, 61, 62**

[a] Isolation and identification probably reflects a bias, based upon the quantity and ease of isolation of these compounds and the availability of plant sources. Very likely, there are many more undiscovered glucosinolates.

linkages in various oxidation states. The largest single group (one-third of all glucosinolates) contain a sulfur atom in various states of oxidation (e.g. methylthioalkyl-, methylsulfinylalkyl-, or methylsulfonylalkyl). Another small group of benzyl glucosinolates have an additional sugar moiety, rhamnose or arabinose, in glycosidic linkage to the aromatic ring. The presence of these sugars is of unknown significance, although it is intriguing that they are present in two families of plants (the Moringaceae and Resedaceae) containing certain genera that are widely exploited for their pharmacological properties. There has been an unconfirmed report that the 5-carbon sugar, apiose, may be linked to the hydroxybenzyl glucosinolate side chain in *Hesperis matronalis*, a member of the Brassicaceae family (Larsen et al., 1992; Halkier, 1999). Additionally, a number of sinapoyl and cinnamoyl salts and esters of some of the common glucosinolates are substituted on the thioglucoside moiety (Linscheid et al., 1980; Sakushima et al., 1995). Bjerg and Sørensen (1987) claim that cinnamoyl derivatives of glucosinolates predominate in some plants and plant parts, and they present hypothetical structures of *p*-coumaroyl, caffeoyl, feruloyl, sinapoyl and isoferuloyl glucosinolates with these phenylpropenyl moieties esterified to the S-β-glucose at positions C-2′ and C-6′. These compounds are not discussed further in this review. With few exceptions, the configuration at chiral centers of a number of the compounds represented in Fig. 1 is not fully characterized.

3.2. Isolation and crystallization

Early isolations of glucosinolates used paper and thin-layer chromatography almost exclusively (Greer, 1962; Bjorkman and Janson, 1972). High voltage electrophoresis combined with paper chromatography has been used, but with low yield and considerable complications (Elliott and Stowe, 1970; Wetter and Dyke, 1973; Olsen and Sørensen, 1980a). This early work is reviewed by Olsen and Sørensen (1981). Isolations of indole and aryl glucosinolates have been reported in which acidic alumina was used as the initial step, followed by either ion exchange chromatography on DEAE–Sephadex A-25 (Hanley et al., 1983) or Sephadex G10 size exclusion chromatography (Hanley et al., 1984). Excellent results in isolating preparative quantities of diverse glucosinolates from crude extracts, by reversed phase (C-18) solid phase extraction or flash-chromatographic reversed phase techniques are described in detail by Bjerg and Sørensen (1987) and Peterka and Fenwick (1988). A disadvantage of most of this work, however, was that the products were rarely of established purity and crystallized. Thies (1988) described a method by which gram quantities of glucosinolates can purportedly be obtained rapidly. Although this paper provides explicit and easy to understand protocols for two glucosinolates (sinigrin and glucotropaeolin), crystallizing other glucosinolates still remains problematic. Very few additional glucosinolates have therefore been crystallized (Thies, 1988). Early attempts to isolate naturally occurring glucosinolates included the crystallization of sodium salts of 2-hydroxy-2-methylpropyl glucosinolate and of the tetraacetate and pentaacetate (derivatives of the thioglucoside moiety) forms of this compound (Kjær et al., 1956; Schultz and Wagner, 1956). Kjær listed nine glucosinolates that had been crystallized as either potassium, sodium or rubidium salts, and another seven that had been characterized as crystalline acetates by the year 1959 (Kjær, 1961).

3.3. Chemical synthesis

Although methods for the synthesis of a number of glucosinolates (e.g. benzyl-, methyl-, phenethyl-, 2-propenyl-, 3-butenyl-), were reported over four decades ago (Ettlinger and Lundeen, 1957; Benn, 1963, 1964a–c; Benn and Ettlinger, 1965; Benn and Yelland, 1967; Kjær and Jensen, 1968; Matsuo, 1968), these compounds were not routinely synthesized, nor is their synthesis straightforward. Synthetic routes to naturally occurring indole glucosinolates have recently been developed by Rollin and colleagues (Viaud and Rollin, 1990; Viaud et al., 1992; Chevolleau et al., 1993; Gardrat et al., 1993). Gram-scale synthetic protocols were developed for phenethyl glucosinolate in 1980 (Gil and MacLeod, 1980e), a milligram-scale synthesis for ethyl glucosinolate (Keller et al., 1984), the gram-scale synthesis of sinigrin (Abramski and Chmielewski, 1996), and the first synthesis [milligrams] of ω-methylthioalkyl glucosinolates, 2-methylthioethyl-, 3-methylthiopropyl- and 4-methylthiobutyl-glucosinolate (Mavratzotis et al., 1996) have been reported. Synthesis of a group of α-glucosinolates (e.g. anomers of the naturally occurring phenyl-, benzyl-, 2-phenethyl- and indol-3-ylmethyl-glucosinolates, as well as (*E*)-styryl glucosinolate which has not been found to occur naturally) was reported by Blanc-Muesser et al. (1990). Other analogues (e.g. deoxyglucotropaeolins and 2-fluoro-2-deoxyglucotropaeolins) were synthesized to establish the importance of the OH group at carbon-2 for glucosinolate–myrosinase binding but also to study the molecular mechanism of this reaction (Cottaz et al., 1996, 1997). Further, Lazar and Rollin (1994) developed a glucosinolate analog in which the anionic OSO_3 was replaced by an OPO_3^2 moiety, in order to observe the changes in myrosinase hydrolysis kinetics after alteration of a site deemed critical in the glucosinolate recognition process. Most recently, Aucagne et al. (1999) have reported the synthesis of "C-glucotropaeolin," benzyl glucosinolate in which the thioglucoside sulfur atom is replaced by a carbon. Rollin and colleagues, leaders in modern day glucosinolate synthetic chemistry (Blanc-Muesser et al., 1990; Joseph and Rollin, 1993a,b; Lazar and Rollin, 1994; Cottaz et al., 1996, 1997; Aucagne et al., 1999), have reported a new approach to the synthesis of glucosinolate precursors that may broaden the range of synthetically accessible compounds (Cassel et al., 1998). Glucoraphanin, the member of this family of compounds that is to us most interesting from a nutritional standpoint, has not yet been synthesized, but controlled oxidation of glucoerucin to yield glucoraphanin and sulforaphane has been recently reported by Iori et al. (1999), and a series of synthetic analogs of sulforaphane were developed by Posner et al. (1994).

3.4. Biosynthesis

Most of our knowledge of the biosynthesis of glucosinolates is based on elegant studies by Underhill and colleagues at the Prairie Regional Laboratories in Saskatoon, Canada (see Underhill et al., 1973 for details), and more recent genetic studies by Mithen and collaborators at the Institute of Food Research, Norwich, UK (Dawson et al., 1993; Magrath and Mithen, 1993; Magrath et al., 1993, 1994; Parkin et al., 1994; Mithen et al., 1995b; Toroser et al., 1995; Giamoustaris and Mithen, 1996). Taken together, this body of work has provided strong evidence that elongation of amino acid side chains (e.g. α-amino acid homologues, derived from common amino acids by acetate addition to the α-keto acid and decarboxylation), occurs before *S*-glycosylation, whereas side chain modification (e.g. desaturation, hydroxylation) probably occurs after addition of the glycone moiety.

The initial step in the biosynthesis of the glucosinolates proceeds, as in that of cyanogenic glucosides, by *N*-hydroxylation of a precursor amino acid, followed by decarboxylation to form an aldoxime. In brief, the widely accepted model for glucosinolate biosynthesis involves three major steps: (a) side chain elongation; (b) glucone biosynthesis; and (c) side chain modification. Early evidence for the chain elongation of aliphatic glucosinolates came from in-vivo radiolabelling studies almost 40 years ago. Administration of ^{14}C-labelled amino acids and ^{14}C-acetate to horseradish, nasturtium and watercress resulted in the isolation of ^{14}C-labelled glucosinolates (Underhill et al., 1962; Chisholm and Wetter, 1964). Subsequent studies with *Arabidopsis thaliana* and *Brassica napus* have examined genetic variants in side chain length. This has led to the mapping of a number of "*Gsl-elong*" loci, allelic variation at which has been proposed to determine the length of the glucosinolate side chain, and to the isolation of a yeast artificial chromosome clone that hybridizes to RFLP markers near the *Gsl-elong* gene in *Arabidopsis* (Magrath et al., 1994; Mithen and Campos, 1996).

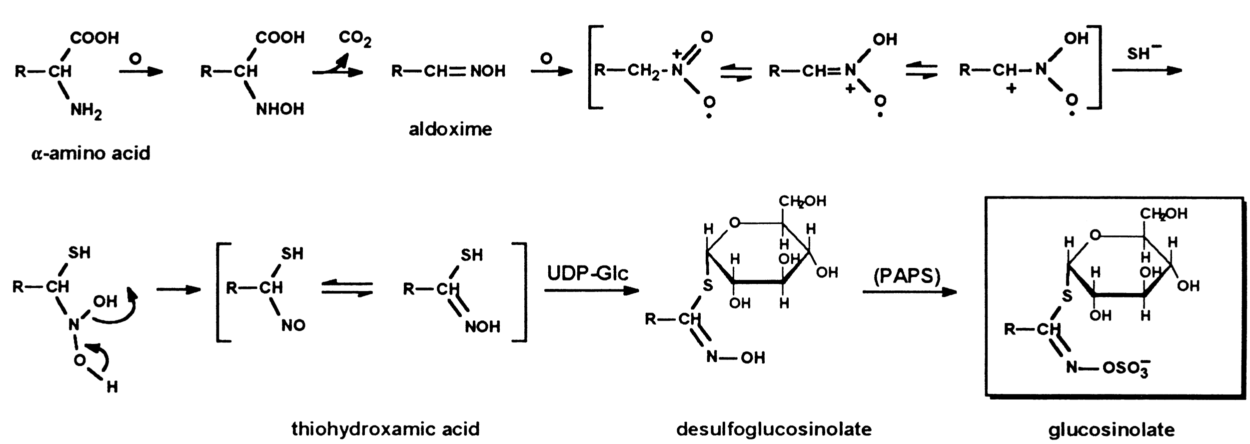
Glycone biosynthesis is initiated by the conversion of protein amino acids (e.g. alanine, methionine, valine, leucine or isoleucine for the aliphatic glucosinolates; phenylalanine or tyrosine for the aromatic glucosinolates and tryptophan for the indole glucosinolates) or chain elongated amino acids (e.g. many of the precursors of aliphatic glucosinolates such as homomethionine, dihomo-methionine, trihomo-methionine) to aldoximes (reviewed by Kjær and Olesen Larsen, 1973, 1976; Halkier and Du, 1997; Halkier, 1999; Mithen et al., 2000). Conclusive evidence has only recently been developed that cytochromes P450 catalyze the conversion of amino acids to aldoximes, a process long known also to be required by cyanogenic glycoside-producing plants (Hull et al., 2000; Wittstock and Halkier, 2000).

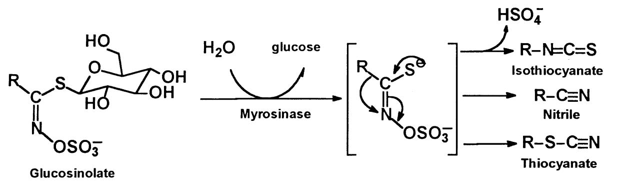
Biosynthetic steps after aldoxime formation are believed to involve conversion to a thiohydroximic acid, introduction of the thioglucoside sulfur from cysteine, *S*-glycosyl transfer from UDP-glucose, and sulfation by the universal high energy sulfate donor, 3′-phosphoadenosine-5′-phosphosulfate [PAPS] (Underhill, 1980; Haughn et al., 1991; Reed et al., 1993; Bennett et al., 1993, 1995; GrootWassink et al., 1994; Halkier and Du, 1997; Du and Halkier, 1998; Witczak, 1999; Halkier, 1999; Mithen et al., 2000). Neither biochemical evidence for the proposed intermediates between aldoxime formation and thiohydroximic acid nor purification and characterization of many of the enzymes in these steps has been attained. *S*-Glycosylation of thiohydroximic acids is catalyzed by a soluble UDPG:thiohydroximate glucosyltransferase and results in a desulfoglucosinolate. This enzyme has been purified from *Brassica napus, B. juncea, B. oleracea* and *Arabidopsis thaliana* (Jain et al., 1990b; Reed et al, 1993; GrootWassink et al., 1994; Guo and Poulton, 1994). Both the *B. oleracea* and the *B. napus* enzyme had high substrate-specificity for thiohydroximates, but had very low specificity for side chain structure. The final step in glycone formation is the sulfation of desulfoglucosinolates. This occurs via a soluble 3′-phosphoadenosine 5′-phosphosulfate (PAPS):desulfoglucosinolate sulfotransferase. This too has been purified and characterized but it is extremely unstable and it has a highly variable and selective substrate specificity (Glendening and Poulton, 1988; Jain et al., 1990a).

The precise mechanism of side chain modification of glucosinolates has been the source of much speculation and little experimental work. Initial oxidation of the side chain sulfur of methionine and its chain elongated homologues is expected to give rise to the large family of methylsulfinyl- and methylsulfonyl-glucosinolates. The Mithen group has proposed models for side chain modification of aliphatic and alkylthioalkyl glucosinolates based upon allelic variation at three loci: Gsl-oxid, Gsl-alk and Gsl-oh, resulting in oxidation (of the methylthio group), desaturation (of alkyl to alkenyl side chains) and hydroxylation (of alkenyl groups) respectively (Parkin et al., 1994; Mithen et al., 1995b; Giamoustaris and Mithen, 1996). Presumably, similar hydroxylations, desaturations and oxidations occur to the branched chain, aromatic and indole glucosinolates since they present a similar range of structural diversity to the aliphatic glucosinolates. The exception to this is the fact that at least ten of the aromatic and indole glucosinolates are singly or multiply methoxylated. It has been suggested that benzoyloxyalkyl glucosinolates arise from the conjugation of a hydroxylalkyl glucosinolate with benzoic acid (Mithen et al., 2000).

4. Hydrolysis of glucosinolates by plant and microbial myrosinases

Glucosinolates are very stable water-soluble precursors of isothiocyanates, and are typically present in fresh plants at much higher levels than their cognate isothiocyanates. Under carefully controlled conditions designed to extract glucosinolates and isothiocyanates completely, while preventing myrosinase activity, some fresh plants have been shown to contain almost exclusively glucosinolates (Fahey et al., 1997). The relatively nonreactive glucosinolates are converted to isothiocyanates upon wounding of the plant, mastication of fresh plants (i.e. vegetables) or by tissue damage caused by bruising or freeze–thawing during cultivation, harvest, shipping or handling (Bones and Rossiter, 1996; Rosa et al., 1997). This tissue damage releases myrosinase (EC 3.2.3.1), a glycoprotein that coexists with, but is physically segregated from its glucosinolate substrates. Myrosinase has long been thought to be localized in specialized 'myrosin' cells (Bones and Iversen, 1985; Bones et al., 1991; Drozdowska et al., 1992). An abundance of histological and immunochemical evidence (Luthy and Matile, 1984; Lenman et al., 1990; Bones, 1990; Bones et al., 1991; Höglund et al.,





1991; Bones and Rossiter, 1996) suggests that this enzyme is normally sequestered within aqueous vacuoles, although it is present in dormant mature seeds, so that unresolved questions remain about its localization in those organs.

Myrosinase has recently been cloned and sequenced (Xue et al., 1992; Henrissat et al., 1995; Rask et al., 2000) and its X-ray structure has been mapped (Burmeister et al., 1997, 2000). It is a β-thioglucosidase with an amino acid sequence that has strong similarities to that of the glycosylhydrolase family [EC 3.2.1–3.2.3]. The enzyme thus makes contact with the substrate and appears to require an hydroxyl group at C-2 on the glucose moiety for glucosinolate binding. There is a single nucleophilic glutamate (Glu-426), which is required for catalytic activity, in contrast to two glutamate moieties at the active sites of the related family 1 *O*-glycosidases (Cottaz et al., 1996). After hydrolytic cleavage of the β-glucosyl moiety, the sulfate moiety is released nonenzymatically to form the thiohydroxamate-*O*-sulfonate from both aliphatic and aromatic glucosinolates. This unstable intermediate then rearranges to form isothiocyanates, or other breakdown products (e.g. thiocyanates, nitriles, epithionitriles, oxazolidine-2-thiones) in a manner that depends upon the glucosinolate substrate as well as the reaction conditions (e.g. pH, or the presence of Fe^{2+} or epithiospecifier protein). The extensive and confusing literature on myrosinase products will not be discussed except for those formed from the indole and goitrogenic glucosinolates (see Sections 5.1 and 5.2).

The kinetics of the myrosinase reaction differs widely from species to species, and multiple forms of the enzyme can exist even within the same plant (James and Rossiter, 1991). There are fungal (Reese et al., 1958; Ohtsuru and Hata, 1972) and bacterial myrosinases (e.g. *Enterobacter cloacae*; Tani et al., 1974), in addition to the plant enzymes. Myrosinases are also present in many bacteria commonly associated with human and animal gut microflora (Campbell et al., 1987; Diedrich and Kujawa, 1987; Nugon-Baudon et al., 1988, 1990; Rabot et al., 1993) and in the crucivorous aphids *Brevicoryne brassicae* and *Lipaphis erisimi* (MacGibbon and Beuzenberg, 1978). An early report of the occurrence of myrosinase-like activity in mammalian tissues (Goodman et al., 1959) probably reflects the activities of the intestinal microflora, a hypothesis that is strongly supported by recent evidence from a number of laboratories (Oginsky et al., 1962; Rabot et al., 1993; Shapiro et al., 1998; Getahun and Chung, 1999). Myrosinases are activated to various degrees by ascorbic acid, and in some instances the enzyme is almost inactive in its absence (Shikita et al., 1999). Activation is not dependent on the redox reactivity of ascorbate, however, and it has been suggested that ascorbate provides a nucleophilic catalytic group (Ettlinger et al., 1961; Burmeister et al., 2000). The activation of ascorbate is "uncompetitive," i.e. ascorbate raises both V_{max} and K_m for the glucosinolate substrates (Shikita et al., 1999). Myrosinase has been purified and characterized from several sources, including white mustard (*Sinapis alba*; Björkman and Janson, 1972; Palmieri et al., 1986), cress (*Lepidium sativum*; Durham and Poulton, 1989), yellow mustard (*Brassica juncea*; Ohtsuru and Hata, 1972), rapeseed (*Brassica napus*; Lönnerdal and Janson, 1973), and wasabi (*Wasabia japonica*; Ohtsuru and Kawatani, 1979). The enzyme has also been reported to occur in *Raphanus sativus* (daikon) vegetative tissue (Iversen and Baggerud, 1980; El-Sayed et al., 1995) and sprouts (Shikita et al., 1999). Large variations in myrosinase specific activity have been reported in various cruciferous plant sources; Wilkerson and colleagues examined twelve cruciferous vegetables [including red, white, Chinese, and Savoy cabbage, Brussels sprouts, cauliflower, calabrese broccoli, radish, swede, turnip and watercress] and found that the specific activity of partially purified myrosinase ranged from 0.3 μmol/min/mg protein (watercress) to 10.5 μmol/min/mg protein (radish) (Wilkinson et al., 1984). Myrosinase, purified to homogeneity from daikon sprouts, has a specific activity of 280 μmol/min/mg protein with sinigrin as a substrate (Shikita et al., 1999).

To our knowledge only Björkman and Lönnerdal (1973) have evaluated the differential activity of purified myrosinase on a range of different glucosinolate substrates. This work only examined the differential hydrolysis of six glucosinolates, and must be repeated using modern analytical techniques on a wider range of glucosinolates. Evidence strongly suggests, however, that upon ingestion by humans, β-thioglucosidase activity of gut microflora is largely responsible for converting ingested glucosinolates to their cognate isothiocyanates (Shapiro et al., 1998; Getahun and Chung, 1999). Similar observations have also been made in numerous animal studies. For example, presumptive myrosinase activity was demonstrated in chickens (Campbell et al., 1987), rats (Diedrich and Kujawa, 1987; Nugon-Baudon et al., 1990), and in gnotobiotic animals harboring either mixed populations or single bacterial strains of human fecal origin (Nugon-Baudon et al., 1990; Rabot et al., 1993). Almost all of the mammalian chemoprotective activity from crucifers (discussed later in this review) is due to these isothiocyanates. Their formation from glucosinolates by myrosinase is presumably required to generate this biological activity.

Considerable effort has gone into the study of the catabolism of glucosinolates by microbes (Brabban and Edwards, 1994).

5. Glucosinolate content of plants

Glucosinolate content in plants is about 1% of dry weight in some tissues of the *Brassica* vegetables (Rosa et al., 1997), although the content is highly variable (Kushad et al., 1999; Farnham et al., 2000), and can approach 10% in the seeds of some plants, where glucosinolates may represent one-half of the sulfur content of the seeds (Josefsson, 1970). Most species contain a limited number of glucosinolates (generally less than one dozen) although as many as 23 different glucosinolates have been identified in *Arabidopsis thaliana* (Hogge et al., 1988; Haughn et al., 1991). Distribution of the glucosinolates that have been examined varies among plant organs, with both quantitative and qualitative differences between roots, leaves, stems and seeds. For example, seeds or young sprouts of broccoli (*Brassica oleracea* var. *italica*) can contain 70–100 μmol total glucosinolates per g fresh wt, with $<1\%$ contributed by indole glucosinolates and the balance consisting almost entirely of the aliphatic glucosinolates, glucoraphanin, glucoerucin and glucoiberin (Fahey et al., 1997). Late vegetative to reproductive stage plants of the same cultivar typically may contain only about 1–4 μmol of total glucosinolates per g fresh wt, with aliphatic and indole glucosinolates present at roughly equivalent levels (Fahey et al., 1997; Fahey and Stephenson, 1999). A small number of glucosinolates constitute about 0.05–0.1% of the fresh weight of broccoli or about 50–100 mg of glucosinolates per 100 g portion (Kushad et al., 1999; Farnham et al., 2000). Plant age is therefore a major determinant of the qualitative and quantitative glucosinolate composition of plants. Environmental factors such as soil fertility (Booth and Walker, 1992; Fahey and Stephenson, 1999), pathogen challenge (Butcher et al., 1974), wounding (Bodnaryk, 1992) or plant growth regulators (Bodnaryk, 1994; Bodnaryk and Yoshihara, 1995) also have significant effects on levels of specific glucosinolates in the growing plants and may affect distribution among plant organs.

5.1. Special properties of indole glucosinolates

The isothiocyanates formed from indole glucosinolates are unstable, and decompose spontaneously to indole-3-carbinol, indole-acetonitrile, thiocyanate ions and 3,3′-diindolylmethane. Indole-3-carbinol may then spontaneously condense under the acid conditions of the stomach to form compounds that closely resemble 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD, or dioxin) in structure, toxicity and carcinogenicity (Bjeldanes et al., 1991). Despite this toxicity, indole glucosinolate metabolites, in particular indole-3-carbinol, have been investigated for their potential as cancer chemoprotective agents (e.g. Bradlow et al., 1991; Coll et al., 1997). For more detailed treatment of the potentially carcinogenic and anticarcinogenic dual nature of these compounds, see Kim et al. (1997) and reviews by Broadbent and Broadbent (1998a,b), Fenwick et al. (1983), McDanell et al. (1988), Rosa et al. (1997) and Stoewsand (1995).

5.2. Goitrogenic and antinutritional effects of glucosinolates

Hydrolysis of β-hydroxyalkenyl glucosinolates (e.g. progoitrin and epi-progoitrin), gives rise to β-hydroxyalkenyl isothiocyanates. These compounds cyclize to oxazolidine-2-thiones which may have goitrogenic effects in mammals — first observed in rabbits and designated "cabbage" goiter by Webster and Chesney (1930). The "antinutritional" nature of the β-hydroxyalkenyl glucosinolates is discussed in Bille et al. (1983), Vermorel et al. (1988), Mawson et al. (1993a,b, 1994a,b, 1995a,b) and Yong-Gang et al. (1993) as well as in the more general reviews of Fenwick et al. (1983), Rosa et al. (1997) and Griffiths et al. (1998). Efforts to avoid the goitrogenicity of rapeseed (*Brassica napus*), one of the most important oilseed crops in the world, led to the highly successful development of the oilseed crop "Canola." Canola (a contraction of "Canadian" and "oil") was developed in the 1970s by a plant breeding program designed to develop cultivars of oilseed rape with low levels of glucosinolates and erucic acid. The designation "Canola" is not specific, nor does it even refer to a single variety. Two types of Canola are now grown: a short season, yellow seeded, Polish (*Brassica rapa*) type and a longer season, black seeded (*Brassica napus*) variety. Canola seed contains about 40% oil and by regulation this oil must contain $<2\%$ erucic acid. The seed meal, which is fed to animals after oil is expressed, must have <30 μmol of glucosinolates per gram of meal. The value of the Canadian Canola crop now exceeds that of their wheat crop (over 3 million tons produced on about 3 million hectares in Saskatchewan alone, according to the Saskatchewan Canola Development Commission).

5.3. Naturally occurring isothiocyanates outside the plant kingdom

Although isothiocyanates have been reported outside the plant kingdom (e.g. long chain α,ω-bisisothiocyanates from marine sponges; Karuso and Scheuer, 1987), it has been assumed that the route of synthesis in this case is not via glucosinolates (Hagadone et al., 1984). Isothiocyanates from fungi have long been recognized for their antibiotic properties (e.g. paulomycin) but their biosynthesis in fungi appears not to occur through a glucosinolate intermediate (Wiley et al., 1986).

6. Biotic interactions of glucosinolates and isothiocyanates

The antibacterial activities of glucosinolates/isothiocyanates (Kjær and Conti, 1954; Procházka and Komersová, 1959; Virtanen, 1962; Wagner et al., 1965; Dornberger et al., 1975; Johns et al., 1982; Uda et al, 1993; Brabban and Edwards, 1995; Delaquis and Mazza, 1995; Hashem and Saleh, 1999; Lin et al., 2000) and their antifungal activity (Drobinca et al., 1967; Kojima and Ogawa, 1971; Mari et al, 1993; Delaquis and Mazza, 1995; Mayton et al., 1996; Manici et al., 1997; Hashem and Saleh, 1999) have been recognized for many decades. The activity of isothiocyanates such as sulforaphane against numerous human pathogens (e.g. *Escherichia coli, Salmonella typhimurium, Candida* sp.) could even contribute to the medicinal properties ascribed to cruciferous vegetables, such as cabbage and mustard, which have been used as wound poultices and antitumor agents for centuries (Hartwell, 1982). Activity against a range of soil-borne fungal and bacterial plant pathogens is profound, and has been extensively characterized (see reviews by Brown and Morra, 1997; Rosa and Rodrigues, 1999).

Antagonistic interactions are not confined to microbes, since nematocidal activity of glucosinolates has been demonstrated (Lazzeri et al., 1993; Mayton et al., 1996) as has activity as a feeding deterrent to caddisflies, snails and amphipods (Newman et al., 1992). One of the more complex interactions of glucosinolates/isothiocyanates is their activity as allelochemicals, compounds that affect successive plant communities and/or those growing simultaneously, in close proximity (e.g. Brown and Morra, 1995; Charron and Sams, 1999; Smith, 2000). This area has long been the subject of scientific investigation, and has recently been extensively reviewed by Brown and Morra (1997). In addition, glucosinolates are widely recognized as defensive compounds against generalist herbivores and are likely to be involved in host plant recognition by specialist predators, thus acting both as an insecticide and as an insect feeding attractant (e.g. Rodman and Chew, 1980; Louda and Rodman, 1983; Mithen et al., 1986, 1987b; Hammond and Lewis, 1987; Louda et al., 1987; Tsao et al., 1996; Rask et al., 2000). For example, glucosinolates provide important feeding cues to insects including *Pieris* sp. caterpillars and other specialist feeders (e.g. *Plutella* sp., seed weevils, flea beetles), which are differentially stimulated to feed by various glucosinolates (Renwick et al., 1992). Specific tarsal contact chemoreceptors on larvae respond differentially to the glucosinolates rather than the cognate aglycone (e.g. the isothiocyanate) and ovipositing females utilize glucosinolate clues in selecting suitable plants (Rodman and Chew, 1980). Larsen et al. (1992) report that certain glucosinolates found within the host plant (*Hesperis matronalis*) of a monophagous weevil (*Ceutorhynchus inaffectatus*) were powerful feeding stimulants. MacGibbon and Beuzenberg (1978) have demonstrated intense zones of myrosinase activity within the gut of the aphid *Brevicoryne brassicae* that is probably due to bacterial activity. Activity of protective enzymes such as glutathione transferase was induced in *Spodoptera frugiperda* (fall armyworm) and *Trichoplusia ni* (cabbage looper) by feeding on allyl and benzyl isothiocyanates (Chew, 1988). Mithen et al. (1995a) provide insight into the effects of genetically mediated changes in plant chemistry (e.g. glucosinolate content) on plant–herbivore interactions. A synthesis of the extensive literature on insect feeding interactions with glucosinolate-containing plants can be found in Chew (1988), Rask et al. (2000), and in the review by Brown and Morra (1997).

7. Analytical methods

Since the work of Ettlinger and Lundeen (1956a,b, 1957), much effort has been devoted to developing methods for the efficient isolation and identification of glucosinolates (Betz and Fox, 1994). Most early identifications relied on paper or thin-layer chromatography of the glucosinolates or of their presumptive hydrolysis products (e.g. an investigation of the glucosinolates from the seeds of 151 different crucifers by Danielak and Borkowski, 1969). Numerous techniques were utilized for the quantification of "total" glucosinolates. For example, McGregor (1980) examined the environmental and within- and between-laboratory variation of six different analytical methods for glucosinolate determination (e.g. steam distillation and titration of volatile isothiocyanates; UV spectroscopy of oxazolidinethiones; gas chromatography of volatile isothiocyanates; gas chromatography/UV spectroscopy; UV spectroscopy of thiourea derivatives of isothiocyanates; and gas chromatography of trimethylsilyl derivatives of glucosinolates). Glucosinolate separations were then performed by gas liquid chromatography of trimethylsilylated derivatives of glucosinolates from which the sulfate group had been removed (Underhill and Kirkland, 1972a) and this technique was subsequently coupled with mass spectrometry (Christensen et al., 1982). Enzymatic removal of the sulfate prior to derivatization led to multiple products (Heaney and Fenwick, 1987; Theis, 1988). This method was used as recently as 10 years ago by Daxenbichler et al. (1991), who undertook an extensive survey of the glucosinolate composition of seeds from about 300 wild plant species using gas chromatographic detection of desulfoglucosinolate hydrolysis products.

In 1984, G.R. Fenwick and colleagues (Norwich, UK) developed the reversed-phase HPLC method for quantitative analysis of desulfoglucosinolates which is most widely used today (Spinks et al., 1984). This method utilizes an on-column enzymatic desulfation treatment of plant extracts followed by HPLC detection of the resultant desulfoglucosinolates. Adaptation of the sulfohydrolase desulfation method as an HPLC method, although the most widely used method for glucosinolate separation, is still subject to difficulties in interpretation because of the effects of pH, time and enzyme activity on the desulfation products (Minchinton et al., 1982; Spinks et al., 1984; Sang and Truscott, 1984). Typically, this method uses response factors determined with purified desulfosinigrin and uses desulfobenzyl glucosinolate as an internal standard. Correspondence of glucosinolate retention times, and comparison to standardized rapeseed extracts are typically used to validate chromatographic profiles. Unfortunately, the biological activity of these molecules is compromised by the removal of the sulfate. After desulfation, they can no longer serve as substrates for myrosinase and thus their cognate isothiocyanates are not available for bioassay or for direct measurement by cyclocondensation — key tools in the study of the pharmacokinetics, pharmacodynamics and bioactivity of these compounds.

To our knowledge, many plant glucosinolates have not been rigorously identified by modern analytical and spectroscopic methods such as HPLC, NMR, mass spectroscopy or supercritical fluid chromatography with light scattering detection (Fenwick et al., 1980; Eagles et al., 1981; Fenwick et al., 1982; Bjerg and Sørensen, 1987; Bradfield and Bjeldanes, 1987; Lafosse et al., 1990; Prestera et al., 1996). There was, and still is, an extreme paucity of high purity chromatographic standard glucosinolates available to researchers. Only the generosity of a handful of leaders in this field has permitted investigators who do not isolate and purify their own standards to perform meaningful research on these compounds.

7.1. *Characterizing and quantifying glucosinolates (HPLC/MS)*

We have recently improved upon the methods developed by Helboe and others (Helboe et al., 1980; Betz and Fox, 1994) for the separation and identification of individual glucosinolates in plant extracts (Prestera et al., 1996). These improvements exploit: (1) paired ion chromatography of alkylammonium salts (e.g. tetraoctyl- or tetradecylammonium bromide) used in conjunction with myrosinase hydrolysis and isothiocyanate assay by cyclocondensation with vicinal dithiols (Zhang et al., 1992, 1996; see below); (2) a novel method for replacement of the counter ion by NH_4^+ which is critical for bioassay and mass spectroscopy; (3) improvements in mass spectroscopic analysis by combined fast atom bombardment and chemical ionization techniques; and (4) high resolution nuclear magnetic resonance (NMR) spectroscopy, which provides final confirmation of identity (Prestera et al., 1996). This combination of steps provides a powerful method for rapidly characterizing and quantifying glucosinolates.

7.2. *Identifying and quantifying isothiocyanates*

Separation and identification of isothiocyanates from plant extracts is typically accomplished by HPLC (Zhang et al., 1992; Kore et al., 1993; Bertelli et al., 1998). We have also developed a sensitive assay for quantification of total isothiocyanates in plant extracts that exploits the ability of isothiocyanates to react with 1,2-benzenedithiol to form a cyclic thiocarbonyl reaction product, 1,3-benzodithiole-2-thione, with a very high extinction coefficient in the near ultraviolet range (Zhang et al., 1992, 1996). We can now measure as few as 10 pmol of isothiocyanates in complex biological fluids such as plant extracts by modification of this technique for HPLC (Zhang et al., 1996). There is excellent correlation between total glucosinolate titer as determined by measuring isothiocyanates produced by the action of exogenous purified myrosinase on extracted glucosinolates, and the levels of these glucosinolates measured directly by the paired ion chromatography techniques referred to above (Fahey and Stephenson, 1999). This method can therefore be used to quantify either total or individual glucosinolates or isothiocyanates from plant extracts, from separate HPLC peaks or from clinical samples such as urine or blood (Zhang et al., 1996; Fahey et al., 1997; Bertelli et al., 1998; Shapiro et al., 1998; Zhang and Talalay, 1998; Getahun and Chung, 1999).

8. Glucosinolates/isothiocyanates and cancer chemoprotection

Over the past 20 years, compelling evidence has been obtained linking increased consumption of fruits and vegetables, especially cruciferous vegetables, to reduced incidence of many types of cancer (Steinmetz and Potter, 1991, 1996; Block et al., 1992; Doll, 1992; Verhoeven et al., 1996; Michaud et al., 1999; Talalay, 1999). Ingestion of about two servings per day of cruciferous vegetables may result in as much as a 50% reduction in the relative risk for cancer at certain sites (Graham et al., 1978, and as calculated from the data of Kune et al., 1987 and Kohlmeier and Su, 1997). At least some of the cancer chemoprotective activity of these vegetables is widely believed to be due to their content of minor dietary components such as glucosinolates. Certain glucosinolates (e.g. benzyl-, *p*-hydroxybenzyl- and 2-hydroxybut-3-enyl glucosinolates) have themselves been reported to induce mammalian Phase 2 enzymes of detoxication (Wattenberg et al., 1986, Tawfiq et al., 1995; Fahey et al., 1997). The enzyme myrosinase — activated in damaged plant tissue and also present in the microflora of the human digestive tract — converts these glucosinolates to a number of compounds including thiocyanates, nitriles and isothiocyanates. Most attention has been focused on the cancer-preventive potential of these metabolites, primarily as inducers of Phase 2 enzymes but with potential antiproliferative, apoptosis-promoting, redox regulatory and Phase 1 enzyme inhibiting roles as well (Zhang and Talalay, 1994, 1998; Barcelo et al., 1996; Nastruzzi et al., 1996; International Life Sciences Institute, 1999; Gamet-Payrastre et al., 2000; Nakamura et al., 2000). A few examples of these cancer-preventive studies follow: (1) Sulforaphane has been shown to elevate levels of mammalian Phase 2 enzymes by ARE (Antioxidant Response Element)-mediated transcriptional activation (Zhang et al., 1992, 1994; Prestera et al., 1993; Talalay et al., 1995; Talalay and Zhang, 1996; Fahey et al., 1997). Sulforaphane reduced the incidence, delayed the appearance of, and reduced the size of tumors in a rat mammary tumor model (Zhang et al., 1994; Fahey et al., 1997), serves as an indirect antioxidant (Fahey and Talalay, 1999), exerts selective cytostatic and cytotoxic effects on human colon cancer cells in vitro (Gamet-Payrastre et al., 1998), inhibits cytochrome P450 (Mahéo et al., 1997; Morel et al., 1997), in particular CYP2E1 (Barcelo et al., 1996) and induces cell cycle arrest and apoptosis in human colon cancer cells in vitro (Gamet-Payrastre et al., 2000). (2) Phenethyl isothiocyanate has been shown to inhibit induction of lung and esophageal cancer in both rat and mouse tumor models (Morse et al., 1993; Stoner and Morse, 1996, 1997; Hecht, 1996; Stoner et al., 1999). These effects correlated well with a reduction in carcinogen–DNA adduct formation and strongly suggested inhibition of cytochromes P450 as a mechanism of action. An analogous effect on NNK metabolism was observed in smokers who consumed watercress (a source of phenethyl glucosinolate) (Hecht, 1999), as well as a significant increase in the glucuronidation of nicotine metabolites, thus suggesting induction of the Phase 2 detoxication enzyme UDP-glucuronosyltransferase activity in humans by phenethyl isothiocyanate (Hecht et al., 1999). Adesida et al. (1996) demonstrated a pronounced antiproliferative effect of phenethyl isothiocyanate metabolites on human leukemia cells in vitro. (3) Crambene (cyanohydroxybutane), glucoiberin and indole-3-carbinol have been shown to elevate quinone reductase and glutathione transferase (Phase 2 detoxication enzymes) and CYP1A (a Phase 1 enzyme) and, in some cases, to do so synergistically; crambene has been identified as the most potent inducer in this system (Staack et al., 1998; Wallig et al., 1998). (4) The metabolism of isothiocyanates in human volunteers has been examined after ingestion of a plant source of sulforaphane (Shapiro et al., 1998), and phenethyl isothiocyanate (Getahun and Chung, 1999), and both studies strongly suggested a role for microflora in the digestive tract in the hydrolysis of glucosinolates to isothiocyanates. Seow et al. (1998) and Fowke et al. (2001a,b) have utilized the cyclocondensation assay developed by Zhang et al. (1992, 1996) in order to follow the metabolism of dietary isothiocyanates and to demonstrate the correlation of urinary isothiocyanate levels with reported cruciferous vegetable intake obtained from food frequency questionnaires, in free living populations in Singapore and the US, respectively.

9. Concluding remarks

The genus *Brassica*, represents only 1 of over 350 genera in the Brassicaceae family which, in turn, is only 1 of 16 families of glucosinolate-containing higher plants (Table 3). Many glucosinolate-containing genera contain plants that have been used for food or medicinal purposes by various cultures for many centuries (e.g. capers, *Capparis spinosa*; wasabi, *Wasabia japonica*; Arugula, *Eruca sativa*; Radish, *Raphanus sativus*) and are currently being investigated for their fungicidal, bacteriocidal, nematocidal and allelopathic properties (e.g. Chew, 1988; Lazzeri et al., 1993; Palada, 1996; Charron and Sams, 1999). The glucosinolates in species such as *Crambe abyssinica* and *Brassica napus* that can be grown as field and row crops are being investigated as sources of starting material for the production of high value fine chemicals (Daubos et al., 1998) as well as for their use as feedstocks and sources of chemoprotective compounds (Barrett et al., 1998). Nutritive value of defatted seed cake from lesser grown glucosinolate-containing plants such as the tropical annual *Cleome viscosa* (already eaten as a leafy green and a condiment) have been explored (Rukmini and Deosthale, 1979). Other tropical and subtropical species have such a compelling ethnopharmacology and such manifold food and medicinal uses that a more rigorous investigation of the properties of their glucosinolates seems promising.

It may thus be of more than academic interest to re-examine some of the "non *Brassica*" glucosinolate-containing plants for their potential pharmacological value — in particular for cancer chemoprotection. Therefore in Appendix A we list the glucosinolate-containing angiosperms. An unconfirmed report of the occurrence of glucosinolates in the common mushroom

(*Agaricus bisporus*; MacLeod and Panchasara, 1983) is omitted. Likewise omitted are reports claiming to have identified glucosinolates in plantain (*Plantago major*; Cole, 1976) and cocoa (*Theobroma cacao*; Gill et al., 1984), because these conclusions were strongly questioned in subsequent more detailed work (Larsen et al., 1983; Bjerg et al., 1987). The glucosinolates of the vegetable *Brassica* species are not listed by species and variety; rather, the reader is referred to the excellent reviews by Fenwick and colleagues (1983) and by Rosa and colleagues (1997) for a detailed treatment of the glucosinolates of *Brassica* vegetables.

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Appendix on next page

Appendix A

Distribution of glucosinolates among plant species[a,b]

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
BATACEAE											Rodman, 1991a
Batis maritima									**43, 28**[c]		Schraudolf et al., 1971
BRASSICACEAE											
Aethionema											
armenum	**73, 82**										Daxenbichler et al., 1991
Alliaria											
petiolata				**107**			**11**				Cole, 1976, Daxenbichler et al., 1991
Alyssoides											
utriculata	**64, 84**			**12**			**23**				Daxenbichler et al., 1991
Alyssum											
alyssoides	**67, 72, 88, 94**			**12, 24, 101**							Daxenbichler et al., 1991
argenteum	**72, 84, 94**										Danielak and Borkowski, 1969, Daxenbichler et al., 1991
bertolonii ssp. *scutarinum*	**72, 94**										Daxenbichler et al., 1991
chondrogynum	**84, 94**										Hasapis et al., 1981
constellatum	**73**										Daxenbichler et al., 1991
dasycarpum				**24**			**23**				Daxenbichler et al., 1991
desertorum	**67, 88**						**23**				Daxenbichler et al., 1991
granatense	**67, 72, 88, 94**			**24**							Daxenbichler et al., 1991
minus	**72, 94**										Daxenbichler et al., 1991
minutum	**67, 72, 88, 94**			**24**							Daxenbichler et al., 1991
murale	**67, 72**										Daxenbichler et al., 1991
peltarioides	**73, 95**										Daxenbichler et al., 1991
perenne			**56**				**12**				Cole, 1976
saxatile	**72, 94, 95**		**56**	**12, 101**			**12**				Cole, 1976, Danielak and Borkowski, 1969
sibiricum	**73, 95**										Daxenbichler et al., 1991
tortuosum	**72, 84, 94**						**105**				Daxenbichler et al., 1991
troodi	**87, 88, 94**										Hasapis et al., 1981
Anastatica											
hierochuntica	**73**										Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Aliphatic Branched- C	Aliphatic Olefins D	Aliphatic Alcohols E	Aliphatic Ketones F	Aromatic Aryl G	Aromatic Benzoate H	Aromatic Indole I	Multiply glycosylated J	Reference
Arabidopsis											
thaliana	**64, 66, 67, 69, 72, 73, 84, 87, 88, 92, 94, 95**		**56**	**12, 107**	**26, 42**		**12, 105**	**5, 6, 10**	**43, 47, 48**		Cole, 1976, Daxenbichler et al., 1991, Haughn et al., 1991, Hogge et al., 1988, Ludwig-Müller et al., 1999
wallichii	**66, 69, 87, 92**			**12, 107**							Daxenbichler et al., 1991
Arabis											
alpina L.	**65, 68, 89, 95**										Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991
var. *grandiflora*	**65, 68**										Daxenbichler et al., 1991
amplexicaulis	**68, 69, 85, 89, 92**						**23, 50**				Daxenbichler et al., 1991
caucasica	**95**										Cole, 1976
drummondii	**67, 72, 78, 88**		**56, 61, 62**		**57**		**11**				Rodman and Chew, 1980
glabra	**66, 67, 87, 88**						**23**				Daxenbichler et al., 1991
hirsuta[f]	**69, 71, 87, 92, 93**		**56**				**50**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Kjær and Schuster, 1972a
ssp. *hirsuta*	**69, 89, 92**						**23, 50**				Daxenbichler et al., 1991
holboellii	**67, 92**		**56, 61**								Daxenbichler et al., 1991
kennedyae	**87, 88, 95**			**107**							Hasapis et al., 1981
laevigata	**69, 82, 87, 92**		**56**	**107**							Daxenbichler et al., 1991
nipponica	**69, 92**						**23, 50**				Daxenbichler et al., 1991
petiolaris				**107**							Daxenbichler et al., 1991
purpurea	**87, 89**										Hasapis et al., 1981
sparsiflora	**66, 67, 87, 88, 94**		**56, 61**				**105**				Daxenbichler et al., 1991
stelleri var. *japonica*	**69, 92, 95**						**23, 50**				Daxenbichler et al., 1991
turrita	**68, 69, 77, 79, 80, 92, 95**										Cole, 1976, Daxenbichler et al., 1991
Armoracia											
lapathifolia Gilib.[g]	**37, 73, 82, 84, 86, 88, 94, 95**	**13, 16, 51, 102**	**54, 55, 56, 61, 62**	**12, 19, 38, 101, 107**	**25, 39, 41**		**11, 44, 103, 104, 105, 106**		**43**		Ettlinger and Kjær, 1968, Fenwick et al., 1983, Grob and Matile, 1980

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Appendix A. (*continued*)

		Aliphatic					Aromatic				
FAMILY	Sulfur-containing	Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
Aubrietia											
deltoidea	**95**		**61**		**57**		**46**	**9**			Ahmed et al., 1972b, Cole, 1976, Danielak and Borkowski, 1969, Kjær et al., 1956, Kjær et al., 1971
Aurinia											
saxatilis	**73, 94**			**12, 101**							Daxenbichler et al., 1991
ssp. *orientalis*	**72, 84, 94**		**61**	**12, 101**							Daxenbichler et al., 1991
Barbarea											
intermedia	**95**		**56**	**107**			**105**				Cole, 1976
orthoceras							**40, 105**				Daxenbichler et al., 1991
praecox									**47**		Danielak and Borkowski, 1969
stricta			**56**	**107**			**105**				Cole, 1976
verna							**23, 105**				Daxenbichler et al., 1991
vulgaris	**95**						**40, 105**		**43, 47**		Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Huang et al., 1994
Berteroa											
incana	**94**			**101**							Cole, 1976
Biscutella											
auriculata	**68, 69**										Daxenbichler et al., 1991
didyma	**64, 95**						**11, 105**				Lockwood and Belkhiri, 1991
laevigata	**68, 69**						**23, 105**				Cole, 1976, Daxenbichler et al., 1991
Boreava											
aptera				**12**			**23**				Daxenbichler et al., 1991
orientalis				**12, 24**			**23**				Daxenbichler et al., 1991
Bornmuellera											
dieckii	**67, 72, 94**						**23**				Daxenbichler et al., 1991
Brassica sp. (predominant GS's)	**63, 64, 72, 73, 84, 94, 95**		**56, 61**	**12, 24a, 38, 100, 101, 107**			**23, 105**		**43, 47**		
Bunias											
orientalis	**63, 64**		**56**				**23**				Daxenbichler et al., 1991
Cakile											
arabica			**56, 61**	**107**							Rodman, 1981
artica	**84, 95**			**12, 107**			**105**				Rodman, 1981
constricta	**84, 94, 95**		**61**	**12, 107**							Rodman, 1981

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Appendix A. (*continued*)

FAMILY	Sulfur-containing	Aliphatic Straight-	Branched-	Olefins	Alcohols	Ketones	Aromatic Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
edentula ssp. *eden* v. *eden, Northern*	**95**		**56, 61**	**12, 107**			**11**				Rodman, 1981
ssp. *eden* v. *eden, Southern*	**73, 95**		**56, 61**	**12, 107**			**11**				Rodman, 1981
ssp. *eden* v. *lacustris*	**95**		**56, 61**	**12, 107**			**11**				Rodman, 1981
ssp. *harperi*	**64, 84, 94, 95**		**61**	**12, 101, 107**			**105**				Rodman, 1981
geniculata	**84, 95**		**61**	**12, 107**							Rodman, 1981
lanceolata ssp. *alacranensis*	**84**			**12**							Rodman, 1981
ssp. *fusiformis*	**84, 94, 95**		**61**	**12, 101, 107**							Rodman, 1981
ssp. *lanceolata*	**84, 94, 95**		**61**	**12, 101, 107**			**105**				Rodman, 1981
ssp. *pseudoconstricta*	**84, 94, 95**		**61**	**12, 101, 107**							Rodman, 1981
maritima	**84, 95**		**56, 61**	**12, 101, 107**			**23**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991
ssp. *baltica*	**95**		**56, 61**	**12, 107**							Rodman, 1981
ssp. *euxina*	**95**			**107**							Rodman, 1981
ssp. *maritima* (W.Med.)	**64, 73, 81, 84, 88, 94, 95**		**56, 61**	**12, 107**							Rodman, 1981
ssp. *maritima* (W.Eur.)	**95**		**56, 61**	**107**							Rodman, 1981
Calepina											
irregularis	**73, 82**										Daxenbichler et al., 1991
Camelina											
microcarpa	**65, 74**										Daxenbichler et al., 1991
rumelica	**65, 68, 74**										Daxenbichler et al., 1991
sativa	**65, 68, 84**										Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Fenwick et al., 1983
Capsella											
bursa-pastoris	**65, 68, 84, 95**			**24, 101, 107**			**23**				Daxenbichler et al., 1991
cordifolia			**56, 61, 62**		**30, 31, 57**		**11, 105**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Lockwood and Belkhiri, 1991
Cardamine											
armara			**54**								Danielak and Borowski, 1969
flexuosa			**56, 61**	**12**			**11, 105**				Daxenbichler et al., 1991
hirsuta			**61**	**12, 101**			**11, 23, 105**				Cole, 1976, Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
impatiens				**12, 101**			**11**				Cole, 1976, Daxenbichler et al., 1991
var. *pectinata*				**12, 101**							Daxenbichler et al., 1991
pratensis			**54, 61**								Cole, 1976, Danielak and Borkowski, 1969
Cardaria											
chalapensis	**64, 67, 72, 84, 88, 94**						**11, 23, 105**				Daxenbichler et al., 1991
draba	**64, 76, 84**	**13**	**61**	**12, 101, 107**			**23**				Cole, 1976, Daxenbichler et al., 1991, Hasapis et al., 1981, Lockwood and Belkhiri, 1991
ssp. *chalapensis*	**64, 67, 76, 88**						**23**				Daxenbichler et al., 1991
Carrichtera											
annua	**72, 84, 94**			**12, 101**							Daxenbichler et al., 1991
Caulanthus											
lasiophyllus	**72, 94**		**56**								Daxenbichler et al., 1991
Cheiranthus											
cheiri	**82, 84**										Cole, 1976, Daxenbichler et al., 1991, Kjær, 1959
kewensis	**73, 95**										Chisholm, 1972
Chorispora											
purpurascens				**12, 24**			**23**				Daxenbichler et al., 1991
tenella	**64, 73, 84, 95**			**107**							Daxenbichler et al., 1991, Rodman and Chew, 1980
Christolea											
crassifolia	**67, 88**		**56, 61**								Daxenbichler et al., 1991
Cochlearia											
anglica			**54, 56, 61**		**31**						Cole, 1976, Kjær et al., 1956
danica			**54, 56, 61**		**31**						Cole, 1976, Kjær et al., 1956
officinalis			**54, 56**		**31**						Ahmed et al., 1972b, Brown and Stuart, 1968, Danielak and Borkowski, 1969, Kjær et al., 1956
Coincya											
longirostra				**12, 24a, 24b, 107**			**23**				Cole, 1976, Vioque et al., 1994

(*continued on next page*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
monensis ssp. *cheiranthos*											Vioque et al., 1994
var. *granatensis*				**12, 24a, 24b**			**23**				Vioque et al., 1994
var. *johnstonii*				**24a, 24b**			**23**				Vioque et al., 1994
var. *recurvata*				**12, 24a, 24b**			**23**				Vioque et al., 1994
var. *setigera*				**24a, 24b**							Vioque et al., 1994
ssp. *nevadensis*				**12, 24a, 24b**			**23**				Vioque et al., 1994
ssp. *orophila*				**12, 24a, 24b**			**23**				Vioque et al., 1994
ssp. *puberla*				**12, 24a, 24b**			**23**				Vioque et al., 1994
rupestris ssp. *leptocarpa*				**12, 24a, 24b**			**23**				Vioque et al., 1994
ssp. *rupestris*				**12, 24a, 24b**			**23**				Vioque et al., 1994
transtagana				**24a, 24b**			**23**				Vioque et al., 1994
Conringia											
orientalis	**95**		**62**	**12, 24**	**31**				**28, 43, 47**		Ahmed et al., 1972b, Boufford et al., 1989, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Gmelin and Virtanen, 1959b, Lockwood and Belkhiri, 1991, Underhill and Kirkland, 1972b
planisiliqua				**12, 107**			**23**				Daxenbichler et al., 1991
Coronopus											
didymus							**11**				Daxenbichler et al., 1991
squamatus							**23, 114**				Daxenbichler et al., 1991
Crambe											
abyssinica				**24b**			**23**				Daubos et al., 1998, Daxenbichler et al., 1965, Daxenbichler et al., 1991
cordifolia				**24**							Daxenbichler et al., 1991
filiformis				**12, 24**			**23**				Daxenbichler et al., 1991
juncea				**12, 24**			**23**				Daxenbichler et al., 1991
koktebelica				**12, 24**			**23**				Daxenbichler et al., 1991
maritima				**12, 24b, 107**			**23**				Danielak et al., 1969, Daxenbichler et al., 1991, Quinsac et al., 1994
orientalis				**12, 24**			**23**				Daxenbichler et al., 1991
tataria				**24**			**23**				Daxenbichler et al., 1991
Dentaria											
laciniata					**29, 31, 57**		**23**				Daxenbichler et al., 1991
Descurainia											
appendiculata				**12, 107**							Daxenbichler et al., 1991
pinnata				**12, 107**							Daxenbichler et al., 1991
ssp. *ochroleuca*				**12, 24, 101, 107**							Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY	Aliphatic					Aromatic				
	Sulfur-containing	Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
richardsonii	**76, 94**		**56, 61, 62**	**12, 101, 107**			**11**				Rodman and Chew, 1980
sophia			**61**	**12, 107**			**23**				Cole, 1976, Daxenbichler et al., 1991
Dimorphocarpa											
wislizenii	**67, 72, 87, 88, 94**										Daxenbichler et al., 1991
Diplotaxis											
catholica				**12**			**23**				Daxenbichler et al., 1991
crassifolia							**23**				Daxenbichler et al., 1991
erucoides	**84, 95**			**12, 107**			**11, 23, 105**		**28, 43, 47, 48**		Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Hasapis et al., 1981, Lockwood and Belkhiri, 1991
griffithii	**64, 84**						**23**				Daxenbichler et al., 1991
muralis				**107**							Danielak and Borkowski, 1969
siifolia				**12, 101**			**23**				Daxenbichler et al., 1991
tenuifolia	**64, 84**										Cole, 1976, Daxenbichler et al., 1991
viminea	**84**		**56, 61**	**107**			**23**				Cole, 1976, Daxenbichler et al., 1991
virgata			**56, 61**	**12, 24**			**11, 105**				Daxenbichler et al., 1991, Lockwood and Belkhiri, 1991
Dithyrea											
californica	**67, 72, 87, 88, 94**			**107**							Daxenbichler et al., 1991
Draba											
aizoides	**84, 95**										Cole, 1976
nemorosa var. *hebecarpa*	**68**		**61**	**12, 107**							Daxenbichler et al., 1991
spectabilis	**69**		**56, 61**								Rodman and Chew, 1980
Enarthrocarpus											
strangulatus				**24**			**23**				Daxenbichler et al., 1991
Erophila											
verna			**56, 61**				**11, 23**				Daxenbichler et al., 1991
Eruca											
longirostris	**64, 84**			**12**							Daxenbichler et al., 1991
sativa	**84, 95**		**61**								Ahmed et al., 1972b, Cole, 1976, Danielak and Borkowski, 1969, Fenwick et al., 1983
vesicaria	**64, 84**										Daxenbichler et al., 1991
ssp. *sativa*	**64, 84**										Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY		Aliphatic					Aromatic				
	Sulfur-containing	Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
Erucaria											
hispanica				**24**			**23**				Daxenbichler et al., 1991
Erucastrum											
gallicum				**12, 107**							Danielak and Borkowski, 1969
laevigatum				**12, 107**			**23, 105**				Daxenbichler et al., 1991
nasturtiifolium	**63**						**23**				Daxenbichler et al., 1991
strigosum	**73**						**23**				Daxenbichler et al., 1991
Erysimum						**99**					Chisholm, 1973
allionii	**64, 76, 82, 84**										Daxenbichler et al., 1991
asperum	**33, 35, 37, 67, 72, 73, 76, 82, 88, 91, 94**		**61**	**107**			**23**	**8**			Daxenbichler et al., 1991, Rodmann and Chew, 1980
aureum	**95**		**61**								Cole, 1976
capitatum	**73, 82**			**107**							Daxenbichler et al., 1991
cheranthoides	**84, 95**										Cole, 1976
cuspidatum	**73, 82**										Daxenbichler et al., 1991
diffusum	**73, 82**										Daxenbichler et al., 1991
hieracifolium	**33, 35, 37, 72, 73, 82, 84, 94, 95**			**107**	**42**						Cole, 1976, Daxenbichler et al., 1980, Daxenbichler et al., 1991, Kjær and Schuster, 1970
linifolium	**73, 82**										Daxenbichler et al., 1991
ochroleucum	**82**					**1**					Danielak and Borkowski, 1969
odoratum	**73**			**107**		**1**[h]					Blua et al., 1988, Chisholm, 1973, Daxenbichler et al., 1991, Kjær and Gmelin, 1957
perofskianum	**64, 76, 82, 84, 95**										Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991
repandum	**73, 84, 95**										Cole, 1976, Daxenbichler, 1991
rhaeticum	**32, 34, 36, 37, 67, 72, 78, 81, 88, 94**										Kjær and Schuster, 1973
rupestre	**82**					**1**					Chisholm, 1973, Danielak and Borkowski, 1969, Kjær and Gmelin, 1957
sisymbrioides	**73, 82**						**23**				Daxenbichler et al., 1991
sylvestre	**73, 95**										Daxenbichler et al., 1991

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Appendix A. (continued)

FAMILY	Sulfur-containing	Aliphatic Straight-	Branched-	Olefins	Alcohols	Ketones	Aromatic Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
Euzomodendron											
bourgaeanum	**64, 95**										Daxenbichler et al., 1991
Farsetia											
aegyptia				**107**							Gil and MacLeod, 1980b
clypeata	**84**										Gil and MacLeod, 1980b
hamiltonii	**64, 72, 73, 84, 94, 95**		**53, 61**	**12, 107**			**11, 105**				Daxenbichler et al., 1991
jacquemontii	**64, 84**		**56**	**12**			**23**				Daxenbichler et al., 1991
ramosissima	**84**			**12**							Gil and MacLeod, 1980b
Fibigia											
macrocarpa	**64**			**12, 24**							Daxenbichler et al., 1991
Goldbachia											
laevigata	**82**						**23**				Daxenbichler et al., 1991
Heliophila											
amplexicaulis	**79, 80**						**23**				Daxenbichler et al., 1991
longifolia							**15, 23**				Daxenbichler et al., 1991
Hesperis											
matronalis	**67, 72, 84, 94, 95**		**61**	**12, 24**			**14, 23, 105**			**119, 120**	Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Larsen et al., 1992
pendula	**67**						**23**				Daxenbichler et al., 1991
Hirschfeldia											
incana	**95**			**12, 24, 101, 107**			**23, 105**				Cole, 1976, Daxenbichler, 1991, Lockwood and Belkhiri, 1991
Iberis											
amara	**73, 84, 95**			**12**							Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Kjær, 1959
crenata	**73, 82**			**12**							Daxenbichler et al., 1991
linifolia	**73, 82**										Daxenbichler et al., 1991
sempervirens	**84, 95**										Danielak and Borkowski, 1969
simplex	**73, 82**										Daxenbichler et al., 1991
umbellata	**73, 95**			**107**							Daxenbichler et al., 1991
Isatis											
aleppica				**12**							Cole, 1976
cappadocica ssp. *steveniana*				**12, 24**			**23**				Daxenbichler et al., 1991
costata				**12, 24**			**23**				Daxenbichler et al., 1991
djurdjura	**64**			**12, 24**					**28, 43, 47, 48**		Lockwood and Belkhiri, 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	 Branched- C	 Olefins D	 Alcohols E	 Ketones F	Aromatic Aryl G	 Benzoate H	 Indole I	Multiply glycosylated J	Reference
glauca				**12**			**23**				Daxenbichler et al., 1991
iberica				**12**			**23**				Daxenbichler et al., 1991
tinctoria	**64, 95**			**12, 24**			**23**		**28, 43, 47, 48, 112**		Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Elliott and Stowe, 1971, Lockwood and Belkhiri, 1991
Leavenworthia											
alabamica					**57**		**23, 105**				Daxenbichler et al., 1991
torulosa				**101**			**105**				Daxenbichler et al., 1991
Lepidium											
apetalum							**11**				Daxenbichler et al., 1991
austrinum	**64**	**16**					**11, 23, 45**				Daxenbichler et al., 1991
bonariense							**46**				Kjær and Wagnières, 1971, Kjær et al., 1971
campestre							**23**				Danielak and Borkowski, 1969
densiflorum							**11, 23**				Daxenbichler et al., 1991
draba	**82**										Danielak and Borkowski, 1969
graminifolium	**95**						**11, 15, 22, 23, 44, 114**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Olsen and Sørensen, 1980a
heterophyllum	**95**										Cole, 1976
hyssopifolium							**11, 114**				Kjær and Wagnières, 1971, Kjær et al., 1971
iberis	**84**										Daxenbichler et al., 1991
lasiocarpum							**11, 23**				Daxenbichler et al., 1991
latifolium	**95**										Cole, 1976
montanum v. *angustifolium*			**56, 61**				**11, 23, 45**				Daxenbichler et al., 1991
perfoliatum	**64, 84, 94, 95**						**11, 45**				Daxenbichler et al., 1991
pinnatifidum							**11**				Daxenbichler et al., 1991
ruderale							**11**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
	Aliphatic						Aromatic				
sativum	**69**			**24, 107**			**11, 23, 105**		**43, 47**		Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Gil and MacLeod, 1980a, Gil and MacLeod, 1980c, Gil and MacLeod, 1980d, Gmelin and Virtanen, 1959a, Schraudolf, 1965
sordidum							**114**				Kjær and Wagnières, 1971
subulatum				**12, 101**			**11, 23, 45**				Daxenbichler et al., 1991
thurberi							**11, 45**				Daxenbichler et al., 1991
vesicarium							**11, 15, 22, 45**				Daxenbichler et al., 1991
virginicum							**11, 23**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991
v. *medium*							**11, 23**				Daxenbichler et al., 1991
Lesquerella											
angustifolia	**64, 84**										Daxenbichler et al., 1991
argyraea ssp. *argyraea*	**73**						**23**				Daxenbichler et al., 1991
auriculata	**67, 88**										Daxenbichler et al., 1991
densipila	**67, 88**										Daxenbichler et al., 1991
douglasii	**82**										Daxenbichler et al., 1991
engelmannii	**64, 76, 84**										Daxenbichler et al., 1991
fendleri	**73**										Daxenbichler et al., 1991
globosa	**73, 84, 95**										Daxenbichler et al., 1991
gordonii	**73**										Daxenbichler et al., 1991
gracilis ssp. *gracilis*	**73, 95**						**23**				Daxenbichler et al., 1991
lasiocarpa ssp. *lasiocarpa*	**67, 88**										Daxenbichler et al., 1991
lescurii	**67, 88**										Daxenbichler et al., 1991
lindheimeri	**73, 95**										Daxenbichler et al., 1991
ludoviciana	**64, 72, 73**		**56**	**107**							Daxenbichler et al., 1991
lyrata	**67, 88**										Daxenbichler et al., 1991
mirandiana	**72**										Daxenbichler et al., 1991
ovalifolia ssp. *ovalifolia*	**67**						**23**				Daxenbichler et al., 1991
perforata	**67, 88**										Daxenbichler et al., 1991
pinetorum	**73, 88**										Daxenbichler et al., 1991
stonensis	**67, 88**										Daxenbichler et al., 1991
tenella	**73**										Daxenbichler et al., 1991
Lobularia											
maritima	**67, 88**			**12, 101, 107**			**11, 105**				Cole, 1976, Daxenbichler et al., 1991, Hasapis et al., 1981

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Appendix A. (*continued*)

		Aliphatic					Aromatic				
FAMILY Genus→species subspecies/variety	Sulfur-containing A	Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
Lunaria											
annua	**67, 94**		**54, 56, 61**								Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Kjær, 1959
rediviva	**64, 66, 67, 69, 72, 84, 94, 95**		**56, 61**	**100, 107**							Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991
Malcolmia											
africana	**64, 67, 72, 73, 82**			**100**			**23**				Daxenbichler et al., 1991
cabulica	**82**										Daxenbichler et al., 1991
littorea	**82, 95**						**23**				Daxenbichler et al., 1991
maritima	**82**				**42**			**10**			Danielak and Borkowski, 1969, Daxenbichler et al., 1980, Daxenbichler et al., 1991
Matthiola											
annua	**63**										Gmelin and Kjær, 1970a
bicornis	**63, 67, 72, 82, 83, 84**										Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Kjær, 1959
fruticulosa	**63, 83, 84**		**56**				**105**				Daxenbichler et al., 1991, Gmelin and Kjær, 1970a
incana	**63, 95**						**105**				Cole, 1976, Gmelin and Kjær, 1970a
parviflora	**63, 83**						**23, 105**				Daxenbichler et al., 1991
sinuata	**63, 83**						**15**				Cole, 1976, Daxenbichler et al., 1991
Moricandia											
arvensis	**95**			**12, 24, 107**			**11, 105**	**6**	**28, 43, 47, 48**		Daxenbichler et al., 1991, Lockwood and Belkhiri, 1991
baetica				**24**			**23**				Daxenbichler et al., 1991
foetida				**24**							Daxenbichler et al., 1991
moricandioides				**24**							Daxenbichler et al., 1991
Nasturtiopsis											
arabica					**29, 31**						Daxenbichler et al., 1991
Nasturtium											
officinale	**66, 69, 87, 89, 92**						**11, 23, 105**				Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Lockwood and Belkhiri, 1991
Nerisyrenia											
camporum	**66, 67, 72, 87, 88, 94**										Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
Neslia											
paniculata	**65, 68, 73, 74, 82**										Daxenbichler et al., 1991, Kjær and Schuster, 1972b
Notoceras											
bicorne	**67, 88, 94**			**12, 24**							Daxenbichler et al., 1991
Peltaria											
alliaceae				**12, 24, 60, 107**							Daxenbichler et al., 1991
angustifolia				**12**			**23**				Daxenbichler et al., 1991
Physaria											
floribunda	**64, 67, 72**		**56**								Daxenbichler et al., 1991
Raphanus											
raphanistrum	**83, 95**			**107**							Cole, 1976
sativus	**63, 64, 75, 83, 95**	**20, 102**	**56, 58, 59**	**19, 107**			**23, 105**			**111**	Ahmed et al., 1972b, Cole, 1976, Daxenbichler et al., 1991, Fenwick et al., 1983, Kjær et al., 1978
var. *caudatus*	**63, 64, 83**		**56**	**107**			**23**				Daxenbichler et al., 1991
Rapistrum											
rugosum	**73, 82, 83, 95**			**12**			**23, 105**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Lockwood and Belkhiri, 1991
ssp. *orientale*	**82**			**12**			**23**				Daxenbichler et al., 1991
Reboudia											
pinnata				**12**			**11**				Daxenbichler et al., 1991
Rhynchosinapis											
hispida				**12, 24**			**23**				Daxenbichler et al., 1991
longirostra				**24**			**23**				Daxenbichler et al., 1991
monensis							**11**				Cole, 1976
Rorippa											
dubia	**68, 69**						**23**				Daxenbichler et al., 1991
globosa	**66, 68, 69**						**23**				Daxenbichler et al., 1991
hilariana	**69**			**12, 107**			**23**				Daxenbichler et al., 1991
indica	**69, 92**						**105**				Daxenbichler et al., 1991
islandica	**66, 69**			**12**			**23**				Daxenbichler et al., 1991
nasturtium-aquat.							**105**				Cole, 1976
sylvestris	**69, 92**										Daxenbichler et al., 1991
Rytidocarpus											
moricandioides				**24**			**23**				Daxenbichler et al., 1991

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FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic: Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic: Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
Savignya											
parvifloria							**23**				Daxenbichler et al., 1991
Schimpera											
arabica				**12**			**23**				Daxenbichler et al., 1991
Schouwia											
purpurea				**12, 24, 101, 107**					**28**		Ghaout et al., 1991
Selenia											
aurea							**11, 40, 105**				Daxenbichler et al., 1991
grandis				**24**			**23, 105**				Daxenbichler et al., 1991
Sibara											
virginica	**66, 69, 87, 92**						**23, 40, 105**				Daxenbichler et al., 1991, Gmelin et al., 1970
Sinapis											
alba	**84, 95**		**61**	**12, 24, 101**			**11, 23, 105**		**43, 47**		Ahmed et al., 1972b, Cole, 1976, Danielak and Borkowski, 1969, Fenwick et al., 1983, Lockwood and Belkhiri, 1991, Olsen and Sørensen, 1980a, Schraudolf, 1965
arvensis	**73, 79, 80, 82, 95**			**12, 24, 107**			**23, 105**				Cole, 1976, Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Hasapis et al., 1981, Lockwood and Belkhiri, 1991
Sisymbrella											
aspera	**66, 69**			**12**			**23**				Daxenbichler et al., 1991
Sisymbrium											
alliaria				**107**							Danielak and Borkowski, 1969
altissimum	**95**		**56, 61**	**12, 24, 38**	**57**		**23, 105**				Cole, 1976, Daxenbichler et al., 1991
austriacum	**95**			**38**	**57**			**7, 9**			Ahmed et al., 1972b, Cole, 1976, Danielak and Borkowski, 1969, Kjær and Christensen, 1962
ssp. *contortum*					**57**			**9**			Daxenbichler et al., 1991
confertum					**17, 57**		**23**				Daxenbichler et al., 1991
crassifolium					**31, 57**		**23**				Daxenbichler et al., 1991
erysimoides			**56, 61**								Daxenbichler et al., 1991
gariepinum				**24**			**23**				Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
irio			**56, 61**	**24, 38**							Cole, 1976, Daxenbichler et al., 1991
loesilii				**38, 107**	**17, 57**						Cole, 1976, Daxenbichler et al., 1991
officinale			**56, 61**	**38, 107**			**23**				Cole, 1976, Daxenbichler et al., 1991
orientale	**95**			**12, 24, 38**			**11, 23, 105**				Cole, 1976, Daxenbichler et al., 1991, Hasapis et al., 1981
polyceratium					**17, 31, 57**						Daxenbichler et al., 1991
sophia				**107**							Danielak and Borkowski, 1969
strictissimum	**95**		**56, 61**	**38**							Cole, 1976
Stanleya											
pinnata				**12, 24**							Daxenbichler et al., 1991
Sterigmostemum											
incanum	**73, 95**										Daxenbichler et al., 1991
Streptanthella											
longirostris	**64**			**12**			**23**				Daxenbichler et al., 1991
Streptanthus											
arizonicus				**12**							Daxenbichler et al., 1991
Synthlipsis											
greggii	**94**										Daxenbichler et al., 1991
Tchihatchewia											
isatidea	**69**						**23**				Daxenbichler et al., 1991
Teesdalia											
nudicaulis	**73**				**29, 42**		**105**				Cole, 1976, Daxenbichler et al., 1991
Thelypodium											
ambiguum			**61**	**107**							Daxenbichler et al., 1991
brachycarpum	**72**		**61**	**12, 107**			**11**				Al-Shehbaz, 1973
crispum	**64, 72, 76, 84, 94**		**61**	**12, 101, 107**			**11**				Al-Shehbaz, 1973
eucosmum	**84**		**56, 61**	**12, 101, 107**			**11**				Al-Shehbaz, 1973
flexuosum				**24**							Al-Shehbaz, 1973
howellii ssp. *spectabilis*	**95**		**56**	**12, 101**			**11**				Al-Shehbaz, 1973
integrifolium ssp. *affine*				**24**							Al-Shehbaz, 1973
ssp. *complanatum*				**24**							Al-Shehbaz, 1973
ssp. *gracilipes*				**24**							Al-Shehbaz, 1973
ssp. *integrifolium*				**24**							Al-Shehbaz, 1973
ssp. *longicarpum*				**24**							Al-Shehbaz, 1973
laciniatum	**72, 84, 94**		**56, 61, 62**	**12, 101, 107**			**11, 105**				Al-Shehbaz, 1973
laxiflorum	**84**		**56, 61**	**12, 101, 107**			**11, 105**				Al-Shehbaz, 1973

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Appendix A. (*continued*)

FAMILY	Sulfur-containing	Aliphatic					Aromatic			Multiply glycosylated	Reference
		Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole		
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
milleflorum			**56, 61, 62**				**11, 105**				Al-Shehbaz, 1973
paniculatum			**56, 61**	**12, 101, 107**							Al-Shehbaz, 1973
repandum	**72**			**24**							Al-Shehbaz, 1973
rollinsii			**61**	**12, 107**			**11**				Al-Shehbaz, 1973
sagittatum											
ssp. *ovalifolium*			**56, 61**		**30, 57**		**11, 105**				Al-Shehbaz, 1973
ssp. *sagittatum*			**56, 61**		**30, 57**						Al-Shehbaz, 1973
stenopetalum			**56, 61**								Al-Shehbaz, 1973
texanum				**12**							Daxenbichler et al., 1991
wrightii	**72**			**12, 24**			**11**				Al-Shehbaz, 1973
Thlaspi											
alpestre					**31, 42**		**23**				Daxenbichler et al., 1991
arvense	**73**			**107**			**11**				Danielak and Borkowski, 1969, Daxenbichler et al., 1991, Rodmann and Chew, 1980
avalanum					**31**		**23**				Daxenbichler et al., 1991
perfoliatum							**23**				Daxenbichler et al., 1991
Thysanocarpus											
montanum			**56, 61**								Rodman and Chew, 1980
radians	**73**						**23, 105**				Daxenbichler et al., 1991
Turritis											
glabra	**95**			**107**							Cole, 1976
Wasabi											
japonica	**67**	**51**	**56, 58, 61**	**12, 18, 19, 101, 107**			**105**				Fenwick et al., 1983, Fuke et al., 1997
Zilla											
spinosa				**24**			**23**				Daxenbichler et al., 1991
BRETSCHNEIDERACEAE											Rodman, 1991a
Bretschneidera											
sinensis					**31**		**14**				Boufford et al., 1989
CAPPARACEAE											Rodman, 1991a
Boscia											
fischeri		**51**									Kjær and Thomsen, 1963b
senegalensis		**51**									Seck et al., 1993
Capparis											
angulata						**96**					Kjær and Thomsen, 1963b
baducca		**51**									Gremlin and Kjær, 1970d
cartilagenea		**108**[d]	**54, 56**								Fenwick et al., 1983, Kjær and Thomsen, 1963b

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
ferruginea						**97**					Brown and Stuart, 1968
flexuosa		**13, 51**	**56**	**12, 24**	**25, 26**	**97**	**11**				Ahmed et al., 1972b, Brown and Stuart, 1968, Gaind et al., 1975, Gmelin and Kjær, 1970d, Kjær and Schuster, 1971
galeata			**54, 56**								Kjær and Thomsen, 1963b
grandis					**113**						Gaind et al., 1975
hastata		**51**									Gmelin and Kjær, 1970d
inermis		**13, 51**		**12, 24**	**25**						Kjær and Thomsen, 1963b
linearis				**52**							Brown and Stuart, 1968, Gaind et al., 1975, Kjær and Wagnières, 1965
masaikai					**27**						Hu et al., 1989
Mitchellii			**54, 56**								Kjær and Thomsen, 1963b
nobilis		**51**									Kjær and Thomsen, 1963b
odoratissima		**51**									Gremlin and Kjær, 1970d
ovalifolia		**51**									Kjær and Thomsen, 1963b
ovata											
var. *deserti*									**47**		Ahmed et al., 1972a
var. *palaestina*	**73**	**51**		**107**	**29**	**97**			**43**		Ahmed et al., 1972a, Ahmed et al., 1972b
quiniflora		**51**									Kjær and Thomsen, 1963b
rupestris		**51**									Kjær and Thomsen, 1963b
salicifolia						**97, 98**					Brown and Stuart, 1968, Kjær and Thomsen, 1962b, Kjær and Thomsen, 1963a, Kjær and Thomsen, 1963b
spinosa	**73**	**51**		**107**	**29**	**97**	**23**		**28, 43, 47, 48**		Daxenbichler et al., 1991, Kjær and Thomsen, 1962a, Kjær and Thomsen, 1963b, Shraudolf, 1989
var. *aegyptia*	**73**	**51**		**107**	**29**	**97**					Ahmed et al., 1972a, Ahmed et al., 1972b
var. *deserti*	**73**	**51**		**107**	**27**	**96**			**47**		Ahmed et al., 1972a, Ahmed et al., 1972b
Tuereckheimii		**51**									Kjær and Thomsen, 1963b
Tweediana		**51**									Kjær and Thomsen, 1963b

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
Cleome											
anomala					**29**		**23**		**43, 47**		Daxenbichler et al., 1991, Schraudolf, 1965
arabica		**51**			**29**		**23**				Daxenbichler et al., 1991, Kjær and Thomsen, 1963b
arborea		**51**			**29**				**43, 47**		Ahmed et al., 1972b, Kjær and Thomsen, 1963b, Schraudolf, 1965
diandra					**17, 29, 31**						Daxenbichler et al., 1991
gigantea		**51**			**29**						Kjær and Thomsen, 1963b
graveolens		**51**			**29**				**43, 47**		Ahmed et al., 1972b, Kjær and Thomsen, 1963b, Schraudolf, 1965
gynandra[e]											Daxenbichler et al., 1991
integrifolia		**51**			**29**						Kjær and Thomsen, 1963b
isomeris							**23**				Daxenbichler et al., 1991
machycarpa		**51**			**29**						Kjær and Thomsen, 1963b
monophylla		**51**							**43, 47**		Ahmed et al., 1972b, Kjær and Thomsen, 1963b, Schraudolf, 1965
ornithopodioides		**51**			**29**						Kjær and Thomsen, 1963b
papillosa							**23**				Daxenbichler et al., 1991
pilosa		**51**			**29**						Daxenbichler et al., 1991
pungens		**51**									Kjær and Thomsen, 1963b
rosea		**51**									Kjær and Thomsen, 1963b
serrulata		**51**			**29**						Daxenbichler et al., 1991
sonorae							**23**				Daxenbichler et al., 1991
speciosissima		**51**			**29**						Kjær and Thomsen, 1963b
spinosa		**51**			**29**						Kjær and Thomsen, 1962a, Kjær and Thomsen, 1963b
tenuis					**29**		**23**				Daxenbichler et al., 1991
trachycarpa[e]											Daxenbichler et al., 1991
trachysperma		**51**			**29**				**43, 47**		Ahmed et al., 1972b, Kjær and Thomsen, 1963b, Schraudolf, 1965
viscosa		**51**			**29**		**23**				Hasapis et al., 1981, Kjær and Thomsen, 1963b, Rukmini and Deosthale, 1979
Courbonia											
virgata							**23**				Daxenbichler et al., 1991

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic: Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic: Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
Crataeva											
roxburghii		**51**									Kjær and Thomsen, 1963b
tapia		**51**			**29**		**23**				Daxenbichler et al., 1991, Kjær and Thomsen, 1963b
Dhofaria											
macleishii		**51**									Lüning et al., 1992
Dipterygium											
glaucum		**51**									Lüning et al., 1992
Gynandropsis											
gynandra		**51**							**43, 47**		Ahmed et al., 1972b, Hasapis et al., 1981, Kjær and Thomsen, 1963b, Schraudolf, 1965
pentaphylla		**51**							**43, 47**		Kjær and Thomsen, 1963b, Schraudolf, 1965
speciosa		**51**									Kjær and Thomsen, 1963b
Isomeris											
arborea		**51**									Blua and Hanscom, 1986, Blua et al., 1988
Maerua											
aethiopica		**51**									Kjær and Thomsen, 1963b
hoehnelii		**51**			**29**						Kjær and Thomsen, 1963b
ovalifolia		**51**			**29**		**23**				Daxenbichler et al., 1991
pubescens[e]											Kjær and Thomsen, 1963b
Polanisia											
dodecandra					**29**		**23**				Daxenbichler et al., 1991
ssp. *tracysperma*					**29**						Daxenbichler et al., 1991
viscosa					**29**		**23**				Daxenbichler et al., 1991
Puccionia											
macradenia		**51**									Lüning et al., 1992
Ritchiea											
albersii		**51**									Kjær and Thomsen, 1963b
Thylachium											
africanum		**51**									Kjær and Thomsen, 1963b
thomasii		**51**									Kjær and Thomsen, 1963b
Wislizenia											
refracta							**23**				Daxenbichler et al., 1991

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Appendix A. (*continued*)

		Aliphatic					Aromatic				
FAMILY	Sulfur-containing	Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
CARICACEAE											Rodman, 1991a
Jarilla											
chocola							**11**				Daxenbichler et al., 1991, Gmelin and Kjær, 1970b
Carica											
cauliflora							**11**				Gmelin and Kjær, 1970b
chilensis							**11**				Gmelin and Kjær, 1970b
papaya							**11**				Blua et al., 1988, Chan et al., 1978, Flath and Forrey, 1977, Gmelin and Kjær, 1970c, MacLeod and Pieris, 1983, Tang, 1973, Tang, 1974
pennata							**11**				Gmelin and Kjær, 1970b
quercifolia							**11**				Gmelin and Kjær, 1970b
Cycliomorpha											
solmsii							**11**				Tang and Hamilton, 1976
EUPHORBIACEAE											
Drypetes (syn. *Putranjiva*)											
roxburghii			**56**		**29**						Ahmed et al., 1972b, Benn and Meakin, 1965, Kjær and Thomsen, 1963b
gossweileri					**26**						Ettlinger and Kjær, 1968
GYROSTEMONACEAE											Rodman, 1991a
Codonocarpus											
continifolius			**61**								Kjær and Malver, 1979
Tersonia											
brevipes			**61, 62**								Kjær and Malver, 1979
LIMNANTHACEAE											Rodman, 1991a
Limnanthes alba var. *alba*					**31**						Boufford et al., 1989, Daxenbichler and Van Etten, 1974
douglasii							**45**				Ettlinger and Lundeen, 1956b
MORINGACEAE											Rodman, 1991a
Moringa oleifera (syn. *aptera, pterygosperma*)			**56, 61, 62**		**31**		**11, 23**			**3, 110**	Daxenbichler et al., 1991, Kjær et al., 1979, Sørensen, 1970
peregrina			**61, 62**				**11**			**3, 110**	Kjær et al., 1979

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Appendix A. (*continued*)

FAMILY Genus→species subspecies/variety	Sulfur-containing A	Aliphatic Straight- B	Branched- C	Olefins D	Alcohols E	Ketones F	Aromatic Aryl G	Benzoate H	Indole I	Multiply glycosylated J	Reference
PENTADIPLANDRACEAE											Rodman, 1991a
Pentadiplandra											
brazzeana							**11, 49**				El Migirab et al., 1977, Fenwick et al., 1983
PHYTOLACCACEAE											
Codonocarpus											
cotinifolia			**61**		**29**		**23**				Daxenbichler et al., 1991
Phytolacca											
americana							**23**				Daxenbichler et al., 1991
dioica							**11, 22, 23**				Daxenbichler et al., 1991
PITTOSPORACEAE											Rodman, 1991a
Bursaria spinosa var. *incana*							**23**				Daxenbichler et al., 1991
RESEDACEAE											Rodman, 1991a
Caylusea											
abyssinica							**23, 40**				Daxenbichler et al., 1991
Reseda											
alba					**31**		**23, 105**		**43**		Boufford et al., 1989, Daxenbichler et al., 1991, Olsen and Sørensen, 1979, Schraudolf, 1965, Underhill and Kirkland, 1972b
complicata									**43, 47**		Schraudolf, 1965
crystallina									**43**		Schraudolf, 1965
lutea							**11, 23**		**43**		Cole, 1976, Daxenbichler et al., 1991, Schraudolf, 1965
luteola							**23, 40, 105**		**43**		Bjỏrkqvist and Hase, 1988, Cole, 1976, Daxenbichler et al., 1991, Ettlinger and Kjær, 1968, Kirkland et al., 1971, Kjær and Gmelin, 1958
media							**11, 22, 105**		**43**		Olsen and Sørensen, 1980b
odorata							**21**		**43**	**109**	Ahmed et al., 1972b, Olsen and Sørensen, 1979
phyteuma							**23**		**43**		Daxenbichler et al., 1991, Schraudolf, 1965
stricta							**23, 105**				Daxenbichler et al., 1991
Sesamoides canescens var. *canescens*							**40, 105**			**4**	Olsen et al., 1981
pygmaea							**105**				Olsen et al., 1981

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Appendix A. (*continued*)

		Aliphatic					Aromatic				
FAMILY	Sulfur-containing	Straight-	Branched-	Olefins	Alcohols	Ketones	Aryl	Benzoate	Indole	Multiply glycosylated	Reference
Genus→species subspecies/variety	A	B	C	D	E	F	G	H	I	J	
SALVADORACEAE											Rodman, 1991a
Salvadora											
persica							**11, 23**				Daxenbichler et al., 1991
pendula			**56**								Ahmed et al., 1972b
TOVARIACEAE											Rodman, 1991a
Tovaria											
pendula			**56**				**11**		**2, 43, 47**		Chistensen et al., 1982, Schraudolf, 1965, Schraudolf and Bauerle, 1986
TROPAEOLACEAE											Rodman, 1991a
Tropaeolum											
boliviense			**56, 61**				**11**				Kjær et al., 1978
cochabambae			**56, 61, 62**				**11, 46**				Kjær et al., 1978
hjertingii							**11**				Kjær et al., 1978
longiflorum			**56, 61**				**11**				Kjær et al., 1978
majus							**11, 23, 46**				Daxenbichler et al., 1991, Kjær et al., 1978
minus							**11**				Kjær et al., 1978
peregrinum		**16**	**56, 61, 62**		**31**		**11, 23, 46**				Daxenbichler et al., 1991, Ettlinger and Kjær, 1968, Kjær et al., 1978
seemannii			**56, 61**				**11**				Kjær et al., 1978
tuberosum			**56, 61**				**11**				Kjær et al., 1978

[a] Descriptions of many of the compounds specifically referenced herein may also be found in Fenwick et al. (1983), Ettlinger and Kjær (1968) and Kjær and Olesen Larsen (1973, 1976). The taxonomic designations provided by the original authors have not been altered to reflect changes in the taxonomic literature that have occurred since initial discovery, nor have they been adjusted to concur with the International Code of Botanical Nomenclature (1993), since this would make it too confusing for those interested in checking the original references.

[b] Danielak and Borkowski (1969) provide numeous tentative identifications, not all of which are included in this summary. They report finding glucosinolates in a total of 151 cruciferous species, but provide only R_f values (thin-layer chromatography) for many of these.

[c] Schraudolf et al. (1971) describe an hydroxyindole of ambiguous identity.

[d] The designation of *n*-propyl glucosinolate [**108**] by Fenwick et al. (1983) appears to be incorrect since the original reference (Kjær and Thomsen, 1963b) indicates a structure consistent with the name isopropyl glucosinolate [**56**].

[e] Total glucosinolates reported, but no specific compounds identified.

[f] "MeSOcOx" and "MeSOOcOx" reported, but structure not clarified.

[g] "iso-Heptyl" [**115**] and "iso-hexyl" [**116**] reported, but structure not clarified (see Table 1).

[h] 4-Acetylbutyl glucosinolate (glucoerypestrin or 3-methoxycarbonylpropyl glucosinolate, [**1**]) reported in *E. odoratum* or *E. rupestre* — confusion exists about identity of source (see Chisholm, 1973).

[i] The level of analytical resolution provided in most of the studies cited herein does not permit discrimination between progoitrin (**24a**) and epiprogoitrin (**24b**). Clear exceptions are: (a) the well documented predominance of **24b** in *Crambe abyssinica* and *C. maratima*; (b) the well documented presence of **24a** in many *Brassica* sp., especially rapeseed (*B. campestris* and *B. napus*); (c) a report of the presence of both **24a** and **24b** in numerous *Coincya* species (Vioque et al., 1994). With these three exceptions, we have therefore not distinguished between enantiomorphs and use the designation "**24**".

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