COMPREHENSIVE REVIEWS

# Health-Affecting Compounds in Brassicaceae

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ABSTRACT: *Brassicaceae* vegetables are considered to be a staple food in many areas all over the world. *Brassica* species are not only known for their high fat and protein contents for human and animal consumption, but *Brassicaceae* vegetables are recognized as a rich source of nutrients such as vitamins (carotenoids, tocopherol, ascorbic acid, folic acid), minerals (Cu, Zn, P, Mg, among others), carbohydrates (sucrose and glucose), amino acids (for example, L-alanine, L-aspartic acid, L-glutamic acid, L-glutamine, L-histidine, L-methionine, L-phenylalanine, L-threonine, L-tryptophan, and L-valine), and different groups of phytochemicals such as indole phytoalexins (brassinin, spirobrassinin, brassilexin, camalexin, 1-methoxyspirobrassinin, 1-methoxyspirobrassinol, and methoxyspirobrassinol methyl ether), phenolics (such as feruloyl and isoferuloylcholine, hydroxybenzoic, neochlorogenic, chlorogenic, caffeic, *p*-coumaric, ferulic, and sinapic acids, anthocyanins, quercetin, and kaempferol), and glucosinolates (mainly glucoiberin, glucoraphanin, glucoalyssin, gluconapin, glucobrassicanapin, glucobrassicin, gluconasturtiin, and neoglucobrassicin). All of these phytochemicals contribute to the reported antioxidant, anticarcinogenic, and cardiovascular protective activities of *Brassica* vegetables. However, not all members of this family are equal from a nutritional viewpoint, since significant qualitative variations in the phytochemical profiles of *Brassica* species and varieties suggest differences in the health-promoting properties among these vegetables. In this article, *Brassica* phytochemicals with their nutritional value and health-promoting activities are discussed to give an overview of the literature for *Brassica* as a staple crop.

#### Introduction

The Brassicaceae (Cruciferae) family is composed of 350 genera and about 3500 species (Sasaki and Takahashi 2002), including some crops of great economical importance such as Brassica napus L., Brassica rapa L., and Sinapis alba L. (O'Callaghan and others 2000; Onyilagha and others 2003). These species are used as food, spices, and as a source of vegetable oils (Kaushik and Agnihotri 2000). The Brassicaceae vegetables represent a major part of the human diet (Verkerk and others 1997) being consumed by people all over the world (Font and others 2005; Sardi and Tordai 2005; Ferreres and others 2007) and are considered important food crops in China, Japan, India, and European countries (Heaney and Fenwick 1995; Sasaki and Takahashi 2002; Kusznierewicz and others 2008). Over the past 3 decades, *Bras*sica production has grown steadily becoming an important source of oil and protein of plant origin for animal and human nutrition, respectively. Rapeseed (canola) ranks currently as the 3rd source of vegetable oil (after soy and palm) and the 3rd leading source of oil meal (after soy and cotton) (Thiyam and others 2004). Brassica is an inexpensive, though very nutritive, source of food, providing nutrients and health-promoting phytochemicals such as phenolic compounds, vitamins (Dekker and others 2000; Vallejo and others 2002, 2003, 2004), phytic acid, fiber, soluble sugars (Pedroche and others 2004), glucosinolates (Fowke and others

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2003), minerals, polyphenols (Heimler and others 2005), fat, and carotenoids (Figure 1) (Zakaria-Rungkat and others 2000). There is currently much interest in identifying phytochemicals with useful biological activity in food (Rice-Evans and others 1997), and any significant finding related to the presence of valuable compounds in *Brassica* species will be welcomed by the food industry (Thiyam and others 2004).

There is ever-increasing evidence that a higher consumption of *Brassica* vegetables, for example, broccoli, cabbage, kale, mustard greens, Brussels sprouts, and cauliflower, reduces the risk of several types of cancer (Kristal and Lampe 2002; Wang and others 2004). The anticarcinogenic effect of these vegetables has been attributed to decomposition products of glucosinolates, indoles, and iso-thiocyanates (Zukalova and Vasak 2002), phytoalexins, and other antioxidants (Samaila and others 2004; Hanf and Gonder 2005). Indole-3-carbinol, a natural component of *Brassica* vegetables (Staub and others 2002), has an interesting anticarcinogenic potential, acting via different metabolic and hormonal pathways (Hanf and Gonder 2005) and have been proved to reduce the incidence of tumors in reproductive organs (Staub and others 2002) and the growth of human breast cancer cells (Cover and others 1998).

Overall, to date, the most promising anticarcinogenic dietary compounds have been detected in cruciferous vegetables and further elucidation of their protective mechanisms and the identification of other active constituents may contribute to the development of highly health-supporting *Brassica* varieties (Steinkellner and others 2001). Extracts of the different species of the *Brassicaceae* family show antioxidant effects (Azuma and others 1999) and decrease oxidative damage (Ferguson 1999), while

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the juice of some *Brassica* species has been proved to protect human hepatoma cells from the genotoxic effects of carcinogens (Steinkellner and others 2001). However, compounds such as glucosinolates and phytates may also have a negative effect on human and animal health. For example, glucosinolates and glucosinolate by-products can be toxic and are responsible for the bitter, hot, and pungent flavors of *Brassicaceae* vegetables (Kopsell and others 2003). Also, thiocyanates, isothiocyanates, and oxazolidine-2-thiones have been shown to be goitrogenic (Mithen and others 2000), and while *Brassicaceae* vegetables can be a good source of minerals, some antinutrients, such as phytates, can decrease their bioavailability (Matthaus and Angelini 2005).

The purpose of this article is to provide an overview of healthaffecting compounds identified in the *Brassica* genus.

#### Vitamins

*Brassica* vegetables contain high levels of vitamins (Heimler and others 2005), including carotenes, tocopherols (Kurilich and others 1999), vitamin C, and folic acid (Verhoeven and others 1996) (Table 1). It is a well-known fact that the first 3 vitamins have the potential to prevent and treat malignant and degenerative diseases (Kurilich and others 1999). Broccoli (*Brassica oleracea*) extracts are protective against reactive oxygen species

(ROS) presumably due to the presence of vitamin C, quercetin, kaempferol, lutein, zeaxanthin (Kurilich and others 2002),  $\alpha$ -tocopherol,  $\gamma$ -tocopherol, and  $\beta$ -carotene (Eberhardt and others 2005). Bioavailabilty is a critical feature in the assessment of the role of these compounds in human health. When 200 g of broccoli were consumed by healthy volunteers, significant changes, in serum, in both men and women were observed only for lutein, whereas for  $\gamma$ -tocopherol a significant change was detected in women only, whereas no changes were observed for  $\alpha$ -tocopherol,  $\beta$ -carotene, and retinol (Granado and other 2006).

#### Carotenoids

In some *Brassica* species, carotenoid content is 2-fold higher than in spinach (Miyazawa and others 2005). Sixteen carotenoids were identified by Wills and Rangga (1996) in *B. chinensis*, *B. parachinensis*, and *B. pekinensis*, out of which lutein and  $\beta$ -carotene were the most abundant (Riso and others 2003). Lutein has also been isolated from extracts of fresh raw kale (*Brassica oleracea var. Acephala*) (Khachik and others 1999) and high levels of other carotenoids, mainly  $\beta$ -carotene, were also detected (Kurilich and others 1999; Kopsell and others 2003; Lefsrud and others 2006). Two other vegetables, Brussels sprouts and green cabbage, have been reported to contain significant amounts of *trans-\beta*-carotene and *cis-\beta*-carotene (Podsedek

Table 1 -	- Variation of	f vitamins ( $\mu$ g/g)	among different	Brassicaceae	vegetables of	on fresh weight basis.
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	Ascorbic acid	α-Carotene	β-Carotene	α-Tocopherol	Folate
Broccoli	$748\pm62^{a}$	0.3 <sup>b</sup>	8.9 <sup>b</sup>	16.2 <sup>b</sup>	1.771 <sup>d</sup>
Kale	186 <sup>e</sup>	0.6 <sup>b</sup>	48.6 <sup>b</sup>	19.2 <sup>b</sup>	_
Cauliflower	$499\pm53^{a}$	_	$72\pm0.5^{g}$	1.7 <sup>b</sup>	0.53 <sup>e</sup>
Chinese cabbage	253 <sup>a</sup>	_	0.1 <sup>c</sup>	0.8 <sup>c</sup>	0.81 <sup>f</sup>
White cabbage	188 ± 13 <sup>a</sup>	0.02 <sup>b</sup>	0.8 <sup>b</sup>	1.7 <sup>b</sup>	_
Brussels sprouts	158 <sup>c</sup>	_	1.4 <sup>c</sup>	1.5 <sup>c</sup>	-
<sup>a</sup> Bahorun and others 2004. <sup>b</sup> Kurilich and others 1999.					

<sup>o</sup>Kurilich and others 1999. <sup>c</sup>Singh and others 2007. <sup>d</sup>McKillop and others 2002. <sup>e</sup>Boonstra and others 2002. <sup>f</sup>Devi and others 2008. <sup>g</sup>Singh and others 2001.

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2005). Carotenoids present in dark green leafy vegetables might be involved in the prevention of several diseases related to oxidative stress (Riso and others 2003).

#### **Tocopherols**

The predominant tocopherol in all *Brassica* vegetables is  $\alpha$ tocopherol with the exception of cauliflower, which predominantly contains  $\gamma$ -tocopherol (Piironen and others 1986). The to copherol content of rapeseed oil consists of 64%  $\gamma$ -to copherol, 35%  $\alpha$ -tocopherol, and less than 1% is the mixture of  $\delta$ tocopherol and plastochromanol-8 (Goffman and Mollers 2000).

#### Vitamin C

High levels of vitamin C have been reported in Chinese cabbage, broccoli, cauliflower, and cabbage (Bahorun and others 2004) (Table 1). The content of this vitamin in different cultivars of cabbage (Brassica oleraceae L.) ranges from 12 to 112.5 mg/100 g (Goldoni and others 1983).

#### Folic acid

Raw broccoli (McKillop and others 2002), cauliflower (Boonstra and others 2002), and cabbage contain folic acid (Puupponen-Pimia and others 2003) (Table 1), a scarce and important vitamin that acts as a coenzyme in many single carbon transfer reactions in the synthesis of DNA, RNA, and protein components (Devi and others 2008). Folic acid reduces the risk of neural tube defects (NTDs) and may be associated with the reduced risk of vascular disease and cancer (Bailey and others 2003; Cornel and others 2005), while low-folate intake has been identified as a main cause of anemia (Bollheimer and others 2005).

#### Minerals

Brassica plants have been found to be rich in many minerals including calcium and iron (Miyazawa and others 2005). Among the green leafy vegetables, B. oleracea L. acephala (kale) is an excellent source of minerals (Kopsell and others 2003), accumulating high levels of P, S, Cl, Ca, Fe, Sr, and K (Table 2) (Tirasoglu and others 2005). Broccoli accumulates Se to concentrations many times above that found in soil, which may greatly enhance its health-promoting properties (Finley 2003). Different Brassica vegetables such as cauliflower, bok choy (B. rapa) stems and leaves, broccoli (B. oleracea v. botrytis), and kale (B. oleracea v. acephala) are reported to have high mineral contents (Puupponen-Pimia and others 2003) (Table 2). Interestingly, all these Brassica vegetables exhibit excellent calcium bioavailability (Heaney and others 1993). Cabbage leaf (B. oleracea var. *capitata*) also contains potentially useful amounts of copper, zinc, iron, and a number of other essential minerals and trace elements (Glew and others 2005).

Brassica can be cultivated under hydroponic conditions such that lead to high levels of nutritionally important minerals such as Cr, Fe, Mn, Se, and Zn. Owing to reproducible and high concentration of minerals in the edible plant tissue small quantities of this enriched plant can be processed to make capsules or tablets that supply 100% of the recommended daily intake of these elements, with the advantage of using a natural plant source (Elless and others 2000). However, the bioavailability of some of these minerals might be reduced by the presence of glucosinolates, phytates, and phenolics (Matthaus and Angelini 2005)

Heavy metals (for example, Mo, B, Co, Se, Cd, Pb, Cr, Ni, Hg, and As) and others such as Cu, Zn, Mn, and Fe may be found in high concentration in contaminated soils and have toxic effects on plants, animals, and human beings (He and others 2005). The use of metal-accumulating plants to remove toxic metals from soil is known as phytoremediation (Salt and others 1995) and Brassica species such as B. oleracea and B. napus, known for their metal accumulator properties, are used for this purpose (Banuelos 2006). However, this characteristic, which constitutes an advantage for the former use entails, an important toxicological risk if these fruits and vegetables grown in contaminated soils are ingested (Dudka and Miller 1999).

#### Lipids

Rapeseed oil is one of the most common edible oils in the world. Its nutritive value is excellent due to its unsaturated fatty acid content (Naczk and others 1998). Mustard oil is also a significant source of unsaturated fatty acids containing about 94.2%, and only 5.4% saturated fatty acids. These are recognized as essential dietary elements with important effects on human health (Choudhury and others 1997). Mustard oil contains linolenic acid, 21.4% (omega-3); palmitic acid, 2.9%; palmitoleic acid, 0.2%; stearic acid, 1%; oleic acid, 19.4%; linoleic acid (omega-6), 9.7%; and erucic acid, 44.4% (Dwivedi and others 2003), showing an inhibition of mutagenicity (Choudhury and others 1997). Oil content in seeds of different *B. campestris* genotypes varies from 38.9% to 44.6% and major fatty acids found are oleic, linoleic, linolenic, eicosaenoic, erúcic acid ranging from 10.1% to 17.3%, 5.9% to 14.5%, 5.2% to 15.0%, 7.7% to 13.7%, and 39.6% to 59.9%, respectively (Ahuja and others 1989). Canola seed oil is one of the richer sources of omega-3-unsaturated fatty acids (Hanf and Gonder 2005) and, in particular, of  $\alpha$ -linolenic acid (Vermunt and others 2001). The oil of commercial B. napus L. is rich in oleic acid and contains moderate levels of linoleic and linolenic acid (Adamska and others 2004).

Cauliflower is considered to be a food of high nutritional value and some authors relate its quality to the stability of its fatty acids. Environmental stress may enhance the fatty matter content (linolenic acid) and polyphenols (Scalzo and others 2007).

Γable 2–Variation of minerals ( $\mu$ g/g) among	g different <i>Brassicaceae</i>	e vegetables on fresh	weight basis
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	Broccoli	Kale	Cauliflower	Chinese cabbage	White cabbage	Brussels sprouts
Ca	$272\pm20^{a}$	$2860 \pm \mathbf{430^{b}}$	175 ± 17 <sup>a</sup>	$470\pm60^{b}$	$440\pm60^{ m b}$	$356\pm13^{a}$
Fe	$8.7\pm0.5^{a}$	$4\pm2^{b}$	$5.0\pm0.3^{a}$	$2\pm0.3^{b}$	$1.4\pm0.3^{ ext{b}}$	$7.6\pm0.2^{a}$
Cu	$0.94\pm0.07^{\text{a}}$	$0.4\pm0.2^{\text{b}}$	$0.56\pm0.07^{a}$	$0.4\pm0.2^{b}$	$0.5\pm0.5^{ ext{b}}$	$0.9\pm0.09^{a}$
Mg	$181\pm8^{a}$	$510\pm40^{b}$	$145\pm22^{a}$	$130\pm30^{ m b}$	$140\pm20^{b}$	$207\pm12^{a}$
ĸ	$2890\pm70^{a}$	$7120 \pm 5170^{ extsf{b}}$	$2210 \pm 140^{a}$	$2280 \pm 1120^{b}$	$2660\pm870^{\sf b}$	$4250 \pm 250^{a}$
Zn	$9.5\pm0.3^{\text{a}}$	$2.9\pm0.5^{ extsf{b}}$	$6.4\pm0.3^{a}$	$2.3\pm0.4^{b}$	$2\pm1^{b}$	$5.8\pm0.4^{a}$
Na	$180\pm6^{a}$	$120\pm40^{b}$	$192\pm27^{a}$	$50\pm20^{b}$	$30\pm10^{b}$	$107\pm7^{a}$
Mn	$1.92\pm0.09^{\text{a}}$	$3\pm1^{b}$	$1.31\pm0.07^{\text{a}}$	$0.5\pm1.4^{\text{b}}$	$2\pm1^{b}$	$2.31\pm0.13^{\text{a}}$

<sup>a</sup>Kmiecik and others 2007. <sup>b</sup>Kawashima and Soares 2003.

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The essential oil of *B. rapa* var. perviridis leaves was found to contain 48 volatile components, representing 94% to 96.6% of the oil. The main constituents were found to be 3-butenylisothiocyanate (1.4% to 29.2%), 4-pentenyl isothiocyanate (8.2% to 23.5%), 2-methyl 5-hexenenitrile (1.3% to 16.8%), 2-phenylethyl isothiocyanate (7% to 13.7%), and phytol (6.1% to 23.5%) (Miyazawa and others 2005). Volatile chemicals emitted by rapeseed oil also contain monoterpenes (limonene, sabinene,  $\beta$ -myrcene, and *cis*-3-hexen-1-ol acetate), sesquiterpenes, short-chain aldehydes and ketones, other green leaf volatiles, and organic sulfides including the respiratory irritant, dimethyl disulfide (McEwan and Smith 1998). The emission of volatiles from cabbage consisted mainly of monoterpenes (sabinene, limonene,  $\alpha$ -thujene, 1,8-cineole,  $\beta$ -pinene, myrcene,  $\alpha$ -pinene, and  $\gamma$ -terpinene). (Z)-3-Hexenyl acetate, sesquiterpene (E, E)- $\alpha$ -farnesene, and homoterpene (É)-4, 8-dimethyl-1, 3, 7nonatriene were emitted mainly from herbivore-damaged plants (Vuorinen and others 2004).

In *Brassica* oils, triacylglycerols are the main constituents making up about 98% of the oils. The remaining nonglyceridic fraction consists of different lipophylic phytochemicals such as tocopherols, sterols, and sterol esters (Lechner and others 1999). Similarly, in *Brassica* oils the remaining 2% consists of sterols, phospholipids, and sphingolipids. The major sterols were identified as stigmasterol (Appelqvist and others 1981), sitosterol, campesterol, and cholesterol (Lechner and others 1999), the phospholipids as phosphatidylethanolamine and phosphatidylcholine, and the sphingolipids as cerebrosides (Hobbs and others 1996).

For the purposes of human nutrition, a high ingestion of oleic acid and a 2:1 ratio of linoleic:linolenic acid are advantageous (Adamska and others 2004). All polyunsaturated fatty acids including both linoleic and linolenic acids are essential to the human diet because they cannot be synthesized by humans (Ayaz and others 2006). However, the type of fatty acids in the dietary fat is very important, being considered, for example, as one of the detrimental factors in colon cancer development. Fats containing omega-6-polyunsaturated fatty acids were found to enhance chemically induced colon cancer (Dwivedi and others 2003), while omega-3-polyunsaturated fatty acids reduce it (Ferguson 1999; Dwivedi and others 2003). Consumption of diet rich with canola fat may also alter the fatty acid composition of lipids of adipose tissue, muscle, kidney, and liver (Rule and others 1994). A diet high in *trans-* $\alpha$ -linolenic acid may increase plasma LDL/HDL cholesterol and total cholesterol/HDL-cholesterol ratios. Careful deodorization prevents the formation of trans-a-linolenic acid and may help to improve the diet (Vermunt and others 2001).

#### Carbohydrates

The type and concentration of free sugars influence the flavor of *Brassica* products (Rosa and others 2001). Fructose, glucose, and sucrose are the major soluble sugars found in *Brassica* (King and Morris 1994). A comprehensive evaluation of the nutritive profiles of *Brassica* seed meals of yellow-seeded types (*B. napus*, *B. rapa*, *B. juncea*, and *B. carinata*) and conventional brownseeded (canola) type showed that all contain sucrose (7.5% to 8.7%), oligosaccharides (2.3% to 2.5%), ash (6.9% to 7%), and nonstarch polysaccharides (20.4% to 19.7%) (Simbaya and others 1995). Fructose is the major sugar in the different types of *Brassica*, representing between 48.8% and 56.9% of the total sugar content in broccoli cvs. *Marathon* and *Senshi*, respectively, 48.7% (cv. *Mirandela*) and 53.8% (cv. *Murciana*) in the other cabbages. Glucose is the 2nd major sugar, while sucrose represents a maximum of 20.5% in broccoli cv. *Shogun* and 11.1% in cv. *Murciana* (Rosa and others 2001).

#### **Dietary fiber**

It is composed of nonstarch polysaccharides (Knudsen 2001) and is an important constituent in Brassicaceae vegetables, contributing to prevention of colon cancer (Rodriguez and others 2006). În white cabbage (B. oleracea var. capitata) dietary fiber represents one-third of the total carbohydrate content, the other two-third being low-molecular-weight carbohydrates, including glucose (37%), uronic acid (32%), arabinose (12%), and galactose (8%) (Wennberg and others 2002, 2006). The dietary fiber content of 6 cultivars of white cabbage (B. oleracea var. capitata) was evaluated finding that of the average total dietary fiber of 241 mg/g of dry matter, approximately 25% was soluble (Wennberg and others 2002). Dietary fiber content of other species was found to vary between 271 and 352 mg/g for the yellow-seeded B. napus and brown-seeded B. napus, respectively (Slominski and others 1999), with intermediate values in other species, such as cauliflower (302 mg/g DW), broccoli (330 mg/g DW), and cabbage (226 mg/g DW) (Puupponen-Pimia and others 2003).

#### **Protein and Free Amino Acids**

The defatted meal of Brassica oilseeds is a valuable source of protein for the livestock feed industry (Jensen and others 1996) and may constitute an important protein source for human nutrition thereby increasing the value of Brassica crops. However, the high temperatures and organic solvents used during the oil extraction process cause denaturation of proteins in Brassica meal (Pedroche and others 2004). Protein and free amino acid content in rapeseed meal has a high nutritive value, but the utilization of rapeseed/canola as a source of food-grade proteins for human consumption is still limited due to the presence of antinutrients such as glucosinolates, phytates, and phenolics (Mahajan and Dua 1997; Rozan and others 1997; Naczk and others 1998). Therefore, it is used only for animal feeding (Berot and others 2005). There is a variation in protein content in different groups of Brassica, and B. napus seeds have higher protein solubilities than meals from *B. rapa* seeds. Meals with higher protein solubility values also have higher foaming capacity values (Aluko and McIntosh 2001). Seeds of rape, B. napus, and related cruciferous oilseed crops, such as B. campestris, B. juncea, B. carinata, and B. nigra are rich sources of edible protein and rapeseed/canola meal, the by-product of the oil-extraction process, contains up to 42.7% to 50% protein (Simbaya and others 1995; Ghodsvali and others 2005).

The rapeseed (B. napus) meal contains napin and cruciferin as storage proteins and oleosin as a structural protein associated with oil bodies (Berot and others 2005; Ghodsvali and others 2005). The 2S albumins or napins in oilseed rape and turnip rape are potential food allergens (Puumalainen and others 2006). Free amino acids are involved in secondary plant metabolism and in the production of compounds that directly or indirectly play an important role in plant-environment interactions and human health. A total of 17 amino acids were identified (L-alanine, Larginine, L-asparagine, L-aspartic acid, glycine, L-glutamic acid, L-glutamine, L-histidine, L-isoleucine, L-leucine, L-methionine, L-phenylalanine, L-serine, L-threonine, L-tryptophan, L-tyrosine, and L-valine) in B. oleracea var. italica (Gomes and Rosa 2000; Ayaz and others 2006). S-methylcysteine sulfoxide, a naturally occurring S-containing amino acid, is contained at high concentrations in *Brassica* vegetables such as broccoli and cabbage. Its cholesterol-lowering effects have been demonstrated in animals, observing a significant decrease of the serum level of LDL-C (14% decrease) following the oral administration of broccoli (B. oleracea L. var. botrytis L.) and cabbage (B. oleracea L. var. capitata L.) (Suido and others 2002).



Figure 2-Structures of cruciferous phytoalexins: 1: brassinin, 2: brassitin, 3: 1-methoxybrassinin, 4: 4methoxybrassinin, 5: 1-methoxybrassitin, 6: 1-methoxybrassenin A, 7: 1-methoxybrassenin B, 8: cyclobrassinin, 9: cyclobrassinin sulfoxide, 10: cyclobrassinone, 11: dehydro-4-methoxycyclobrassinin, 12: spirobrassinin, 13: 1methoxyspirobrassinin, 14: 1-methoxyspirobrassinol, 15: 1-methoxyspirobrassinol methyl ether, 16: dioxibrassinin, 17: methyl 1-methoxyinodole-3-carboxylate, 18: brassilexin, 19: sinalexin, 20: brassicanal A, 21: brassicanal B, 22: brassicanal C, 23: camalexin, 24: 6-methoxycamalexin, 25: 1-methylcamalexin (Pedras and others 2000).

#### Indoles

Plants may respond to pathogen attack by producing phytoalexins (Morrissey and Osbourn 1999). Phytoalexins are a group of structurally diverse molecules (Grayer and Harborne 1994; Smith 1996) that are generally nonspecific in their antimicrobial activities (Smith 1996; Rogers and others 1996). A number of phytoalexins have been isolated from crucifers (Figure 2) (Pedras and others 2000).

In *Brassica* indole phytoalexin (camalexin) synthesis is induced as a response to pathogen attack and ROS generating abiotic elicitors (Reuber and others 1998; Roetschi and others 2001). These phytoalexins inhibit the growth of human cancer cells and thus may have a potential use as chemopreventive agents (Samaila and others 2004). Several indole phytoalexins found in *Brassica* vegetables, brassinin, spirobrassinin, brassilexin, camalexin, 1-methoxyspirobrassinin, 1-methoxyspirobrassinol, and methoxyspirobrassinol methyl ether, have been found to possess significant antiproliferative activity against various cancer cells, while others, such as cyclobrassinin, spirobrassinin, and brassinin also exhibited chemopreventive activity in models of mammary and skin carcinogenesis (Mezencey and others 2003).

*Brassicaceae* species contain a range of signaling and regulatory compounds known to be involved in general defense mechanisms activated by pathogen and herbivore attacks on plants (Kaplan and others 2004). These include salicylic acid, ethylene,  $H_2O_2$ , and jasmonic acid (an acid-derived oxylipin) (Kurilich and others 1999) and signal peptides, such as systemin (Ryan and others 2002; Ryan and Pearce 2003; Halitschke and Baldwin 2005). Some of these are bioactive compounds that exhibited anticancer activity in animals when added to experimental diets (Kurilich and others 1999). In particular, jasmonic acid and its derivatives, which represent the best characterized class of signal compounds, mediating the defense responses to wounding and herbivore attack in *Brassicaceae* (Creelman and Mullet 1997; Beale and Ward 1998; Blee 1998; Devoto and Turner 2003; Farmer and others 2003), have been proved to inhibit the proliferation of human prostate cancer cells, while not affecting normal human blood cells (Samaila and others 2004; Flescher 2005).

#### Phenylpropanoids, Flavonoids, and Tannins

Flavonoids, hydroxycinnamic acids, phenylpropanoids, and other minor compounds (Table 3) are considered to be among the health promoting compounds in *Brassicacae* species (Pascale and others 2007). Plant polyphenols are multifunctional, having diverse biological activities apart from acting as reducing agents (Rice-Evans and others 1996). Phenolics also contribute to the bitter, astringent, and unpleasant flavor of rapeseed, though the threshold of this unpleasant flavor is higher for individual phenolic compounds than for the mixture (Naczk and others 1998). In spite of this, they are considered to be beneficial and harmless components of rapeseed meal.

The contribution of *Brassica* vegetables to health improvement has generally been associated with their antioxidant capacity and, undoubtedly, phenolic compounds are the major antioxidants of *Brassica* vegetables (Ninfali and Bacchiocca 2003; Podsedek 2005; Singh and others 2006). Phenolics is a generic term that

	Quercetin	Kaempferol	Apigenin	Lutein
Brassica oleracea L. var. Italica (Broccoli)	137 <sup>a</sup>	46 <sup>a</sup>	-	6.8 <sup>c</sup>
Brassica oleracea L. var. botrytis L. (Cauliflower)	39 <sup>a</sup>	12 <sup>a</sup>	2 <sup>a</sup>	1.3 <sup>c</sup>
Brassica campestris var. Chinensis (Chinese cabbage)	390 <sup>a</sup>	96 <sup>a</sup>	45 <sup>a</sup>	0.2 <sup>c</sup>
Brassica rapa L. Subsp. Sylvestris	102 <sup>b</sup>	334 <sup>b</sup>	-	_
Brassica oleracea var. capitata (white cabbage)	51 <sup>a</sup>	-	8 <sup>a</sup>	1.4 <sup>c</sup>

Fable 3 – Variation of ph	enolics ( $\mu$ g/g) among	different Brassicaceae	vegetables on fresh weight basis.
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<sup>a</sup>Bahorun and others 2004

<sup>b</sup>Pascale and others 2007. <sup>c</sup>Singh and others 2007.

refers to a large number of compounds that can be classified in groups, namely, phenolic acids, flavonoids, isoflavonoids, lignans, stilbenes, and complex phenolic polymers (Dewick 2001). As mentioned previously, these antioxidants have proved to be good for human health and also useful as food preservatives (Kroon and Williamson 1999). Mustard seeds have a chemopreventive potential and enhance the antioxidant defence system. Their inclusion in the diet may very probably contribute to reducing the risk of cancer incidence in the human population (Gagandeep and others 2005). A rapeseed phenolic extract has shown a stronger antioxidant activity than many artificial antioxidants (Wanasundara and Shahidi 1994) and exhibited a greater efficiency on a mole-to-mole basis than natural antioxidants such as vitamin C, vitamin E, and  $\beta$ -carotene (Rice-Evans and others

1996). Species of the Brassicaceae family are generally rich in polyphenols. B. rapa (Naczk and others 1998) and B. oleracea L. var. botrytis contain a high amount of phenolic compounds (Llorach and others 2003). Phenolic contents of several species have been reported, such as Chinese cabbage (1189  $\pm$  125  $\mu$ g/g), broccoli (822  $\pm$  89  $\mu$ g/g), cauliflower (278  $\pm$  15  $\mu$ g/g), and white cabbage (153  $\pm$  21  $\mu$ g/g) on a fresh weight basis (Wanasundara and Shahidi 1994; Bahorun and others 2004). In the case of broccoli, hydroxycinnamic acids such as ferulic, sinapic, caffeic, and protocatechuic acids were reported to be the most abundant and important bioactive compounds (Robbers and others 1996; Robbins and others 2005). Four hydroxycinnamic acids (caffeic, p-coumaric, ferulic, and sinapic acid) were identified in the water-soluble phenolic fraction of the leaves of oilseed rape (Brassica napus L. var. oleifera) (Solecka and others 1999) and gallic, protocatechuic, p-hydroxybenzoic, vanillic, syringic, salicylic, *p*-cumaric, caffeic, ferulic, and sinapic acid were identified in kale (B. oleraceae L. var. acephala DC.) (Ayaz and others 2008). The main phenolics in rapeseed meal were determined to be sinapine, which constitutes over 73% of its free phenolic acid content and sinapic acid (Thiyam and others 2004), while rapeseed oil contains vinylsyringol apart from sinapine and sinapic acid (Vuorela and others 2003, 2005). An efficient peroxynitrite scavenger activity has been described for sinapic acid (3,5-dimethoxy-4-hydroxycinnamic acid), which has shown to contribute to the cellular defence against this powerful cytotoxic free radical, thus avoiding peroxynitrite-mediated disorders (Zou and others 2002). Besides the typical seed constituent sinapine, large amounts of choline esters of other phenolic acids have been detected in Brassicaceae species, for example, feruloyl- and isoferuloylcholine and hydroxybenzoic acid (Regenbrechta and Strack 1985). Brassicaceae plants accumulate glucose esters (1,6-di-O-sinapoylglucose), gentiobiose esters (1-O-caffeoylgentiobiose and 1,2,60-tri-Osinapoylgentiobiose) of phenolic acids, and kaempferol conjugates (Alfred and others 2005).

Flavonoids are one of the most common and widely distributed groups of plant phenolics. Over 5000 different flavonoids have

been described to date and they are classified into at least 10 chemical groups. Among them, flavones, flavonols, flavanols, flavanols, anthocyanins, and isoflavones are particularly common in the human diet (Berlin 1997). As these compounds have interesting biological activities, these are being used in numerous medical treatments (Caporale 1995; Morton and others 2000) connected to cancer-prevention (Chu and others 2000, Birt and others 2001) and cardiovascular system protection, including inhibition of oxidative damage (Omenn 1995; Williams and others 2004). At higher doses, however, flavonoids may act as mutagens, pro-oxidants that generate free radicals, and as inhibitors of key enzymes involved in hormone metabolism (Skibola and Smith 2000).

Flavones are involved in various interactions with other organisms, microbes as well as insects and other plants (Sigueira and others 1991). Pharmacological activities have been described for various flavonoids (for example, quercetin, apigenin, catechins), which have shown an anti-inflammatory action by inhibiting cycloxygenase-2 and inducible nitric oxide synthase (Marchand 2002). The flavonols guercetin, kaempferol, and isorhamnetin are among the flavonoid derivatives present in Brassica species (Nielsen and others 1998; Vallejo and others 2002; Onvilagha and others 2003; Chun and others 2004). Two main flavonol glycosides, quercetin 3-O-sophoroside and kaempferol 3-O-sophoroside, are present in broccoli florets. Three minor glucosides of quercetin and kaempferol, isoquercitrin, kaempferol 3-O-glucoside, and kaempferol diglucoside, have also been detected. The quercetin and kaempferol glycosides were present in florets at a level of 43 and 94  $\mu$ g/g DW, respectively (Price and others 1998). Glycosylated kaempferol derivatives from the external leaves of tronchuda cabbage (B. oleracea L. var. costata DC) have been reported by Ferreres and others (2005). Total flavonoid content in Chinese cabbage, broccoli, cauliflower, and white cabbage is 944, 316, 172, and 102  $\mu$ g/g, on a fresh weight basis, respectively (Bahorun and others 2004). Onvilagha and others (2003) reported the accumulation of derivatives of flavonols such as quercetin in Camelina sativa; quercetin and kaempferol in Crambe hispanica var. glabrata; quercetin, kaempferol, and isorhamnetin in Brassica napus; kaempferol and isorhamnetin in Sinapis alba. The constitutive flavonoids of B. napus, isorhamnetin-3-sophoroside-7-glucoside and kaempferol-3,7-diglucoside, are effective deterrents of armyworm (Onyilagha and others 2004). Analysis of B. alba extracts revealed the presence of 3,5,6,7,8-pentahydroxy-4-methoxy flavone in shoots, as well as 2,3,4,5,6-pentahydroxy chalcone and 3,5,6,7,8-pentahydroxy flavone in roots and root exudates. Apigenin was also found in the shoots and roots (Ponce and others 2004).

Anthocyanins are potent antioxidants and consequently may be chemoprotective (Giusti and Wrolstad 2003). *Brassicacae* provide a variety of anthocyanins. Cauliflower and red cabbage showed differences in their anthocyanin profiles: cyanidin-3,5-diglucoside was absent in cauliflower, while it was well represented in red cabbage, together with the characteristic anthocyanin of *Brassica* genus, cyanidin-3-sophoroside-5-glucoside. The *p*-coumaryl and feruloyl esterified forms of cyanidin-3-sophoroside-5-glucoside were predominant in cauliflower, while the sinapyl ester was mostly present in red cabbage (Scalzo and others 2008). Red pigmentation of red cabbage is caused by anthocyanins. Red cabbage contains more than 15 different anthocyanins, which are acylglycosides of cyanidin (Dyrby and others 2001). Red radish (*Raphanus sativus* L.) contains significant amounts of anthocyanins of which 12 acylated anthocyanins were isolated and analyzed spectroscopically to determine their structure. Six of these were identified as anthocyanin glycosides with 1 or 2 hydroxycinnamic acids (Otsuki and others 2002). Total proanthocyanidins content in brocolli was found to be 12 and 7  $\mu$ g/g in cauliflower, calculated over fresh weight (Bahorun and others 2004).

Five lignans, 5 neolignans, 2 sesquilignans, and 1 dilignan were identified in a phytotoxic extract of *Brassica fruticulosa* (Cultillo and others 2003). These compounds exhibited interesting antimicrobial, antifungal, and/or herbicidal activities that are believed to participate in plant defense mechanisms (Erdemoglu and others 2004). These compounds also have cancer-preventive effects (Hanf and Gonder 2005).

Tannins have an adverse effect on the nutritive value of rapeseed meal proteins or isolated proteins (Durkee 1971). These compounds suppress the availability of essential amino acids (Sadeghi and others 2006) and may form complexes with essential minerals, proteins, and carbohydrates (Shahidi 1995). Tannins have also a profound inhibitory effect on the digestion of carbohydrates and proteins in particular (McSweeney and others 2005). In *Brassicaceae* vegetables, different amounts of tannins have been reported (Heimler and others 2005). Inositol hexaphosphate (phytic acid) and condensed tannins are reported in B. carinata (Matthaus and Angelini 2005), both of which play an important role in iron binding (Shahidi 1995). Cabbage and turnip contain various amounts of phytic acid, tannic acid, and/or oxalic acid. Tannic acid was found at 12.66 mg/g (fresh weight basis) in cabbage. Levels of both tannic acid and phytic acid can be significantly (P < 0.05) reduced by different blanching methods (Mosha and others 1995). The total amount of tannins in rapeseed/canola hulls ranged from 19.13 to 62.13 mg/g of oil-free hulls. Insoluble tannins predominated in canola/rapeseed hulls and comprised 70% to 95.8% of total tannins present. The amounts of sodiumdodecyl-sulphate-extractable tannins were comparable to those of soluble tannins but constituted only 4.7% to 14.1% of insoluble tannins present (Naczk and others 2000).

#### Glucosinolates

Sulfur-containing phytochemicals of 2 different types are present in *Brassica* (Cruciferae) vegetables (cabbage, broccoli, and so on): glucosinolates and *S*-methyl cysteine sulfoxide. Glucosinolates (Figure 3) are thioglucosides containing a cyano group and a sulfate group (Zrybko and others 1997).

Glucosinolates are derived from amino acid biosynthesis (Figure 1) and are important secondary metabolites in *Brassicaceae* family, involved in plant defense against pests and diseases (Zrybko and others 1997). For example, glucoiberin, glucoraphanin, glucoalyssin, gluconapin, glucobrassicanapin, glucobrassicin, gluconasturtiin, and neoglucobrassicin are health-promoting compounds found in broccoli inflorescences (*B. oleracea* L., var. *italica*, cv. Marathon) (Vallejo and others 2004). These compounds have both positive and negative nutritional effects (Mithen 2001), appearing to poses anticarcinogenic properties, but also quite different toxicological effects (Stoewsand 1995). The effects of specific glucosinolate degra-



Figure 3 – Basic structure of glucosinolates.

dation products on individual organisms vary and are not always known. If used in excessive quantity, many of these compounds can be highly toxic (Brown and Morra 2005).

Glucosinolates and their concentrations vary among the different groups of Brassicaceae (Table 4) (Windsor and others 2005). In Brussels sprouts, cabbage, cauliflower, and kale, the predominant glucosinolates were found to be sinigrin and glucobrassicin. Brussels sprouts also had significant amounts of gluconapin (Kushad and others 1999). The predominant glucosinolates in broccoli are 4-methylsulfinylbutyl glucosinolate (glucoraphanin) (lori and others 2004), 3-butenyl glucosinolate (gluconapin), and 3-indolylmethyl glucosinolate (glucobrassicin) (Kushad and others 1999). Cruciferous vegetables of the Brassica genus (for example, Brussels sprouts, cauliflower, and broccoli) contain high levels of an indolylmethyl glucosinolate commonly known as glucobrassicin (Rose and others 2005). A great number of glucosinolates have been identified in B. oleracea var. capitata f. alba, namely glucoiberin, progoitrin, epiprogoitrin, sinigrin, glucrafanin, gluconapoleiferin, glucoalisin, gluconapin, 4-hydroxybrassicin, glucobrassicanapin, glucobrassicin, gluconasturein, methoxyglucobrassicin, and neoglucobrassicin (Kusznierewicz and others 2008). The major glucosinolates detected in different varieties of B. oleracea were 2-propenyl, 3methyl-sulphinylpropyl, and indol-3-yl-methyl, which accounted for an average of 35%, 25%, and 29%, respectively of the total glucosinolate content, while in B. rapa, but-3-enyl represented 86% of the total, with pent-4-enyl and 2-phenylethyl as the other major glucosinolates. The average total glucosinolate content of the flower buds was determined to be 2518  $\mu$ mol/100 g DW in troncha (B. oleracea var. tronchuda) and 4979  $\mu$ mol/100 g DW in nabo (B. rapa), which is much higher than the highest amounts reported for broccoli (B. oleracea var. italica) (Rosa 1997). As in other Brassicaceae seeds and plants, rapeseed contains up to 5% of glucosinolates, which are partially decomposed during rapeseed processing or storage. When plant material is crushed, as in food preparation or chewing, a thioglucosidase-mediated autolytic process is initiated, generating indole-3-carbinol, glu-cose, and thiocyanate (Bradfield and Bjeldanes 1991). These, together with other important degradation products, such as isothiocyanates, vinyl-oxazolidinethione, and nitriles, contaminate the crude rapeseed oils, impairing their hydrogenation and transesterification and ultimately may be harmful to human consumption (Velisek and others 1990). The main glucosinolate breakdown products of Brassica vegetables are the sinigrin breakdown product 1-cyano-2,3-epithiopropane, the gluconapin hydrolysis product 3-butenyl isothiocyanate, the glucobrassicin metabolite ascorbigen, and low concentrations of other indole glucosinolate-derived hydrolysis products such as neoascorbigen and 3,3'-diindolylmethane (Smith and others 2005).

Rapeseed meal, a by-product of rapeseed oil production, also contains glucosinolates, which together with phytic acid

	Cabbage	Broccoli	Brussels sprouts	Cauliflower	Kale
Glucoiberin	$2289 \pm \mathbf{380^a}$	$697\pm127^{a}$	$42\pm84^{c}$	-	$3455\pm591^{d}$
Glucoraphanin	17 <sup>a</sup>	$3208 \pm \mathbf{528^a}$	3099 <sup>c</sup>	$218\pm131^{\circ}$	1361 <sup>b</sup>
Progoitrin	$452\pm20^{a}$	$1017\pm68^{a}$	2922 <sup>c</sup>	$120\pm40^{\circ}$	524 <sup>b</sup>
Gluconapin	$472\pm26^{a}$	$96\pm37^{a}$	4654 <sup>c</sup>	$111\pm74^{\circ}$	$372\pm37^{c}$
Sinigrin	$3443 \pm \mathbf{939^a}$	$35\pm143^{c}$	3261 <sup>c</sup>	$3332\pm36^{c}$	$3400\pm322^{d}$
Glucoalysin	_	$90\pm45^{c}$	$90\pm45^{c}$	-	-
Glucoerucin	_	-	_	-	1206 <sup>b</sup>
Glucobrassicin	$1315\pm13^{a}$	$1566\pm130^{a}$	$1431\pm89^{\circ}$	$715\pm716^{\circ}$	$353\pm1029^{\circ}$
Neoglucobrassicin	$38\pm19^{a}$	$458\pm29^{a}$	$95\pm48^{c}$	$95\pm95^{c}$	353 <sup>d</sup>
4-Methoxygluco-brassicin	$214\pm24^{\text{a}}$	$124\pm5^{\text{a}}$	-	-	-

Table 4 – Variation of glucosinolate cont	ents ( $\mu$ g/g) among different <i>Brassicacea</i>	e vegetables on dry weight basis. <sup>A</sup>
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<sup>A</sup>Calculation is made by conversion of  $\mu$ mol to  $\mu$ g on dry weight basis. <sup>a</sup>Verkerk and others 2001.

<sup>b</sup>Kushad and others 2004. Kushad and others 1999

<sup>d</sup>Cartea and others 2008.

contributes to its anti-nutritional properties (Fenwick and Heaney 1983; Tripathi and Mishra 2007). Goitrin, a naturally occurring compound in cruciferous vegetables, can easily be nitrosated if in contact with nitrites in gastrointestinal conditions, yielding the mutagenic compound N-nitroso-oxazolidone, with loss of sulfur (Luthy and others 1984). Additionally, goitrin, which is a decomposition product of progoitrin (Figure 4), is known to be strongly goitrogenic, inhibiting the synthesis of thyroid hormones, thyroxine, and tri-iodine-thyronine by a selective binding of iodine that prevents iodine intake by the thyroid gland (Zukalova and Vasak 2002).

The other decomposion products of glucosinolates, as mentioned previously, are thiocyanates, isothiocyanates, and oxazolidine-2-thiones (Figure 5) (Heaney and Fenwick 1995; Wittstock and Halkier 2002), and have also been shown to be goitrogenic. The benzyl-, phenethy-, allyl-isothiocyanate, and sulforaphane are formed through the hydrolysis of their naturally occurring precursor glucosinolates, glucotropaelin, gluconasturtiin, sinigrin, and glucoraphanin, respectively, by myrosinase (Smith and Yang 2000). However, under certain conditions, the glucosinolate aglycones may yield a nitrile rather than an isothiocyanate. Nitriles such as S-l-cyano-2-hydroxy-3-butene and 1-cyano-2-hydroxy-3,4-epithiobutane are the most toxic of the normal glucosinolate hydrolysis products, with a human lethal dose of 170 and 178 mg/kg, respectively (Fenwick and Heaney 1983). These negative effects of glucosinolates have led to research directed at finding methods to reduce the glucosinolate content in the seeds of some Brassica crops (Font and others 2005). Other processes intended to avoid toxicity of the meal include heat treatment of the seeds prior to removal of the oil. This inactivates myrosinase and subsequent breakdown of glucosinolates when the meal is consumed (Fenwick and Heaney 1983). High or low glucosinolate contents of the seed of some varieties of B. napus correlate positively with glucosinolate levels in the roots, at least during the early stages of in vitro plant development (O'Callaghan and others 2000).

Glucosinolates are also responsible for the bitter acidic flavors of Brassicacea species (Kopsell and others 2003) and the hydrolysis by-products of glucosinolates mentioned previously, such as isothiocyanates, nitriles, and thiocyanates, are responsible for the hot and pungent taste of the mustard that is often objected to by consumers (Zrybko and others 1997). Many of these degradation products are volatile (Valette and others 2006) and also play an important role in the characteristic aroma or off-odor of Brassicacae (Miyazawa and others 2005). A great deal of research has been carried out on the volatiles of these species. Cruciferous vegetables, for example, have been reported to contain substantial quantities of isothiocyanates (Kawanishi and others 2005). Volatiles and semi-volatiles from B. oleracea L. var. botrytis (L.) seeds were identified as cyanides such as 4-(methylthio) butyl-cyanide, 3-(methylthio) propyl cyanide, and isothiocyanates such as 4-(methylthio) butyl-isothiocyanate (Valette and others 2003). In B. rapa L. var. perviridis, 6 isothiocyanates were detected in the steam volatiles and identified as sec-butylisothiocyanate, 3-butenylisothiocyanate, 4-pentenylisothiocyanate, benzyl-isothiocyanate, 2-phénylethylisothiocyanate, and 5-methylthiopentylisothiocyanate. Three nitriles were also detected and identified as 2-methyl-5-hexenenitrile, 3-phenylpropiononitrile, and 6-methylthiohexanonitrile (Miyazawa and others 2005). In Brassica oleracea L. var. Botrytis L. 35 volatile and semi-volatile constituents were detected (Valette and others 2003). Dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, hexanal, 3-cis-hexen-1-ol, nonanal, ethanol (Valette and others 2003; Jacobsson and others 2004), and hex-3(Z)-enol were identified as major constituents representing, respectively, 30.2%, 24.2%, and 21.7% of the volatiles (Valette and others 2003).

Various interesting bioactivities have also been reported for hydrolysis and breakdown products of glucosinolates (O'Callaghan and others 2000; Griffiths and others 2001), such as strong bactericidal, antifungal properties (Fenwick and Heaney 1983; Rosa and others 1997; Tierens and others 2001), and health





promoting effects for plants and humans (Wittstock and Halkier 2002; Font and others 2005). Some of these glucosinolates have a potential application in the industry; for example, an aqueous extract of *B. nigra* seeds might be included in industrial biofilms as an antimicrobial agent (Saraviaa and Gaylardeb 1998). The breakdown products of glucosinolates assist in the activity of important naturally occurring, direct- acting antioxidants such as tocopherols and also enhance the synthesis of glutathione, one of the most abundant intracellular direct antioxidants (Hogge and others 1988; Fahey and Talalay 1999). Working on rapeseed oil cake (*Brassica campestris* L. subsp. *napus*), Nagatsu and others (2004) isolated different antioxidant compounds (indolacetonitrile, S-1-methoxy-1-(3,5-dimethoxy-4-hydroxy-phenyl-acetonitrile), which showed a strong antioxidant activity as evaluated by the ferric thiocyanate method.

Certain glucosinolates, particularly the isothiocyanates and nitriles, have been shown to modify both xenobiotic metabolizing enzymes and induce cell cycle arrest and apoptosis. It is likely that a combination of these responses explains the chemo-preventive characteristics of Brassica and that a combination of different cruciferous vegetables could provide optimal protection (Smith and Yang 2000; Lund 2003). The isothiocyanate chemopreventive activity could be due to its powerful inhibition of different enzymes such as glutathione S-transferases (GSTs) in humans (Seow and others 2002; Ambrosone and others 2004). Another potential cancer-blocking action, which was described for both intact and thioglucoside glucohydrolase-treated glucosinolates, as assessed by induction of GSTs activity, was found to be dependent on the nature of the side chain of the parent glucosinolate (Tawfiq and others 1995). Another naturally occurring isothiocyanate, sulforaphane, that is present in Brassica vegetables has been shown to block the formation of tumors (Liang and others 2005) and together with 7-methylsulfinylheptyl isothiocyanates in broccoli (B. oleracea var. italica) extract exhibited an inhibitory

effect on 12-*O*-tetradecanoylphorbol-13-acetate-induced cancer cell invasion and matrix metalloproteinase-9 activity in human breast cancer cells (Rose and others 2005) and lowers the probability of acquiring colon and rextal cancers (Branca and others 2002). It was also proved to inhibit *Helicobacter pylori* infection, blocking gastric tumor formation. This suggests that broccoli consumption could prevent chronic atrophic gastritis induced by *H. pylori* infection and, thus, this type of stomach cancer (Sato and others 2004). Naturally, the wide range of glucosinolate content among different groups of *B. oleracea* would result in significant differences in their health-promoting properties (Kushad and others 1999).

Indole-3-carbinol (I-3-C) is another glucosinolate breakdown product found in vegetables of the *Brassica* genus (cabbage, broccoli sprouts, Brussels sprouts, cauliflower, bok choy, and kale). Some research points to this compound as a promising anticancer agent against prostate cancer and reducing the incidence and multiplicity of mammary tumors (Hsu and others 2005; Rahman and Sarkar 2005). Coinciding with these studies, oral administration of I-3-C has been shown to have a possible beneficial effect on estrogen metabolism in humans andepidemiological studies support the claim that high intakes of I-3-C may have a broad chemo-preventive effect (Brignall 2001). Conversely, 5,6,11,12,17,18-hexahydrocyclonona[1,2b:4,5-b:7,8-b] triindole (CTr), a major digestive product of indole-3-carbinol, has been proved to exhibit strong estrogenic activities increasing proliferation of estrogen-dependent breast tumor cells. Thus, the contribution of CTr to the cancer preventive or cancerpromoting effects of I-3-C remains to be established (Xue and others 2005). In plants, levels of secondary metabolites, such as glucosinolates are controlled by a number of factors. Although it is possible to increase levels of glucosinolates in plants by genetic manipulation, to enhance a particular pharmacological benefit, such a step would be premature and must await a more thorough understanding of the extremely complex interactions

of these compounds and their metabolites (Heaney and Fenwick 1995).

#### **Future Prospects**

Many anti-cancer agents are of plant origin, but their actual function or the mechanism behind the role they play in the plant has not yet been fully elucidated. For example, plant-derived molecules with known roles in plant cell death may be novel candidates for use in clinical oncology, but a better understanding of the molecular and cellular mechanism of action of such compounds and their structure-activity relationships is necessary for the development of new derivatives of these molecules with more favorable chemopreventive activities. Different classes of anti-cancer compounds merit continued research at a basic and pharmacological level to yield novel chemotherapeutic agents. However, to correctly evaluate the effect of such compounds in food, it is necessary to bear in mind that some constituents such as phenolic acids, tannins, and other anti-nutritional compounds may form complexes with nutritionally important compounds, reducing their bioavailability and thus lowering the nutritional value of Brassica products. Additonal studies are needed to determine the amount of isothiocynates or their metabolites that reach target tissues, and the concentration needed to exert biological effects (Smith and Yang 2000). Further elucidation of the protective mechanisms of food and the identification of active constituents is needed.

Enhancing the phytonutrient content of plant foods through selective breeding or genetic improvement is a powerful tool for dietary disease prevention. However, most, if not all, of these bioactive compounds confer a bitter, acid, or astringent taste to the food, which is rejected by most consumers. Moreover, in the past, some of these compounds have even viewed as plant-based toxins and, as a result, the food industry routinely removes these compounds from plant foods through selective breeding and a variety of debittering processes. This poses a dilemma for the designers of functional foods because increasing the content of bitter phytonutrients for health may clash with consumer choices. Studies on phytonutrients and health, taking sensory factors and food preferences into account, constitute an important area of research.

Another aspect of these valuable *Brassica* vegetables that deserves full attention is the edaphic conditions in which they are grown. These plants can be biofortified by growing them in a high mineral-containing medium, attaining high levels of nutritionally important minerals that can be used to produce dietary supplements. But this advantage, which is due to their metal tolerance (and allows their use for phytoremediation as previously explained), can be negative as observed in crops that are irrigated with polluting metals. The excessive heavy metals (macro or micro nutrients in excess) and plant and human pathogenic microbes concentrated in the soil from this water cause stress conditions for plants. Quality parameters of Brassicacea vegetables are very susceptible to great changes with these stress conditions that produce different effects on the levels of Brassica vegetables metabolites, affecting their flavor and leading to the changes in nutritional value. Studies are needed to clarify the route of exposure, mechanisms of sensitization, and clinical importance of these phenomenons.

Another question about cruciferous vegetables is their flavonoid content. Epidemiological data indicate that the present rate of consumption of these vegetables is beneficial. However, earlier studies also raised the question of the advantages of recommending an increased consumption of Brassica vegetables and/or phytochemical supplements. One of the reasons for this lies in the flavonoid content of these vegetables, which, as explained

previously, is quite high in some of the species. Unfortunately, the potentially toxic effects of excessive flavonoid intake are still largely ignored. It is known that at high doses, flavonoids may act as mutagens, that is, pro-oxidants that generate free radicals, so that their adverse effects may well outweigh their beneficial ones. It is imperative that further research be conducted to learn more about the toxicological properties of flavonoids, apart from other putative health promoting compounds in Brassica vegetables, thus clarifying the balance of potential adverse and beneficial effects included in their mechanisms of action.

#### Conclusions

Brassica vegetables represent a major part of the human diet all over the world providing nutritionally significant constituents, such as phenolic compounds, vitamins, fiber, soluble sugars, minerals, fat, and carotenoids. Cruciferous vegetables are a source of some very promising chemopreventive dietary constituents, which may protect against free radical damage and LDL oxidation implicated in the pathogenesis of cardiovascular diseases, as well as DNA damage and cancer. This might be useful information from the point of view of identifying appropriate raw materials rich in these protective components, for the development of safe food products and additives with appropriate antioxidant properties. As mentioned previously, Brassica plants are rich in many metals including calcium and iron-containing compounds. However, there are substantial variations both within and between subspecies, which suggest a difference in potential health benefits depending on genotype, as well as on the growth conditions and environment. This review provides a massive body of evidence supporting the nutritional value of Brassica vegetables and should ultimately lead the population to better food choices.

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