

Brassicaceae Family

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Brassicaceae family vegetables have an ample worldwide distribution, which can be found in all continents except Antarctica. One of the most striking features of this botanical family is the presence of several kinds of secondary metabolites with a distinctive taste, and also interesting bioactivities. The most deeply studied are the glucosinolates (GSL) and from their bioactive breakdown products, the isothiocyanates and the indoles. Moreover, these species are also rich and possess unique profiles of phenolic compounds, carotenoids, and other groups of less studied compounds such as phytoalexins, terpenes, phytosteroids, and tocopherols, here reviewed.

Bioactive compounds, health-promoters, crucifers

Brassicaceae family vegetables have an ample worldwide distribution, which can be found in all continents except Antarctica [1][2][3][4]. One of the most striking features of this botanical family is the presence of several kinds of secondary metabolites with a distinctive taste, and also interesting bioactivities. The most deeply studied are the glucosinolates (GSL) and their breakdown products, isothiocyanates and indoles [5][6][7]. Moreover, these species are also rich and possess unique profiles of phenolic compounds, carotenoids, and other groups of less studied compounds such as phytoalexins, terpenes, phytosteroids, and tocopherols, here reviewed.

1. Phenolic Compounds

Phenolic compounds are a large class of plant secondary metabolites characterized by having at least one aromatic ring with one or more hydroxyl groups attached, showing a diversity of structures, ranging from rather simple and low molecular weight structures to complex polymeric compounds. More than 8000 phenolic compounds have been reported on plant kingdom [8]. Phenolic compounds are very important regarding the quality of plant-based foods since they are involved in flavor features (e.g., astringency), and they are responsible for the color of some fruits and vegetables and also because they serve as substrates for enzymatic deterioration [9][10]. Finally, phenolic compounds are considered to contribute to the health benefits associated with dietary consumption of *Brassicaceae* species such as antioxidant capacity, anticarcinogenic power, anti-aggregation activity, activation of detoxification enzymes, among others (*Brassicaceae* bioactive properties are reviewed and discussed in Section 3 of the present study). The most important phenolic compounds present in *Brassicaceae* family vegetables are the flavonoids and the hydroxycinnamic acids [8]. Among flavonoids, the most important group corresponds to the flavonols. Quercetin, kaempferol, isorhamnetin, and cyanidin are the most representative flavonols in these species, but their qualitative and quantitative profiles vary significantly among species. For example, cauliflower main phenolic compounds are quercetin aglycon and catechins, but in white cabbage, the main compound are kaempferol glucosides and epicatechins [11][12]. The phenolic profile can also vary within the same plant species according to the plant organ being studied; for example, cruciferous sprouts can contain from 2

to 10 times more phenolic compound when compared with roots and inflorescences, which are the most common plant organ consumed [13]. Recently, Fusari et al. (2019) reported for the first time important levels of *t*-resveratrol -a *p*-terostilbene phenolic compound extensively reported as a potent antioxidant molecule- in several members of this botanical family, reaching, for example, 84 µg/g dry weight level in rocket leaves (*Eruca sativa* L.) [12, 14].

Another group of phenolic compounds frequently detected in *Brassicaceae* vegetables is the hydroxycinnamic acid group, which is characterized by the C6–C3 structure and can be found free or conjugated with sugars or with other acids. The most common in this species are ferulic acid, sinapic acid, caffeic acid, and *p*-coumaric acid, but as occur with flavonols, this varies significantly according to the plant species considered. For example, sinapic acid is the main hydroxycinnamic acid present in rocket salad but is absent in red cherry and daikon radishes [11]. Another example of this considerable variation among species is ferulic acid, which represents the main hydroxycinnamic acid for red cabbage but is absent in radish and rocket leaves [12]. In Figure 1, the chemical structure of the phenolic compounds usually present in *Brassicaceae* is shown.

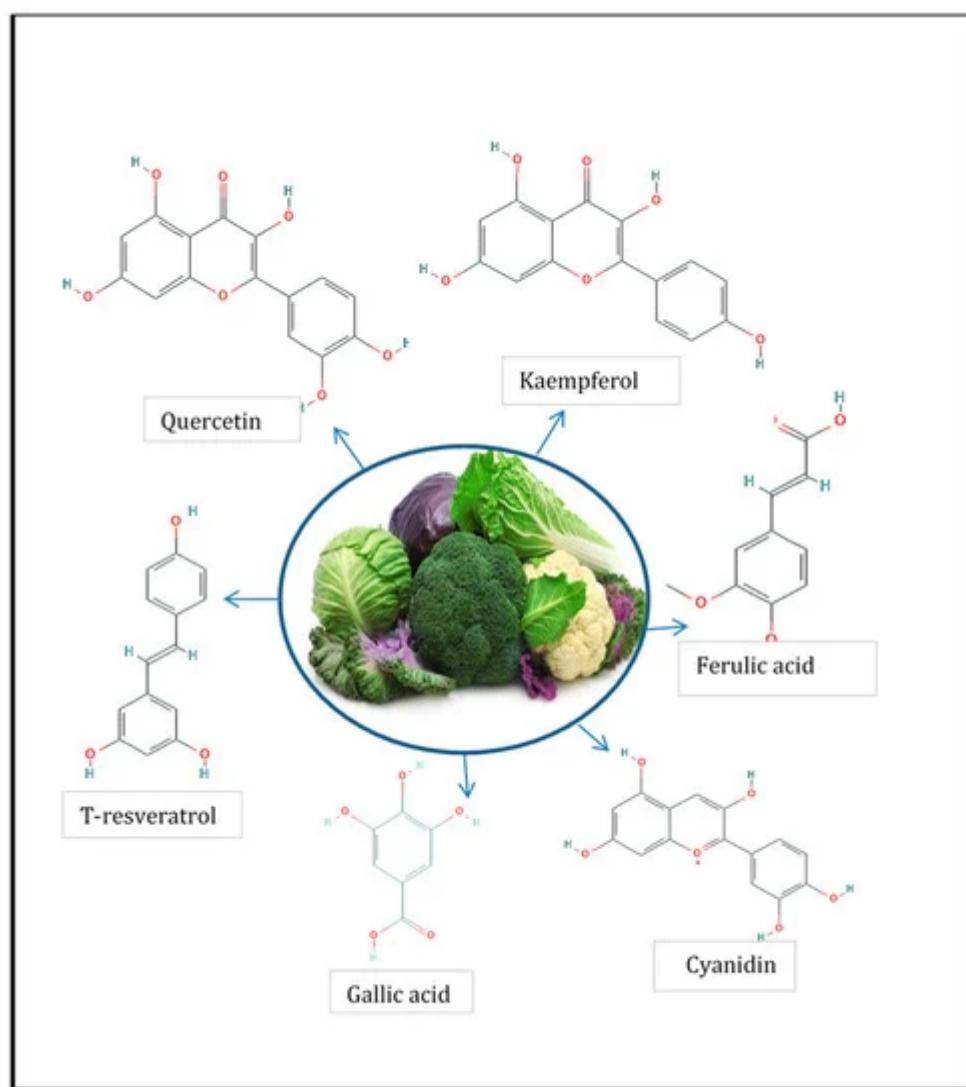


Figure 1. Phenolic compounds present in members of *Brassicaceae* [12].

Anthocyanins have also been reported in *Brassicaceae* vegetables. For example, the red or violet pigmentation of red cabbage, purple cauliflower, or red radishes is caused by anthocyanins. The major type of anthocyanins differs among species. While red radish contains mainly cyanidin and peonidin anthocyanins acylated with aromatic acids [15], red cabbage and broccoli sprouts contain mainly cyanidin glucosides derivatives [16]. Besides, Lo Scalzo et al. (2008) [17] found that the *p*-coumaryl and feruloyl esterified forms of cyanidin-3-sophoroside-5-glucoside were predominant in cauliflower, while the sinapyl one was mostly present in red cabbage. In another study, Otsuki (2002) [18] found 12 different anthocyanins in radish roots, 6 of them corresponding to the pelargonidin derivatives. In red cabbage cultivars, the predominant anthocyanins resulted in being nonacylated cyanidin-glucosides [19]. Altogether, these results indicate that anthocyanins, as with other phenolic compounds, vary according to the vegetable species, the plant organ, and the cultivars of the single species considered.

2. Organosulfur Compounds

Among the organosulfur compounds accumulated by cruciferous vegetables, glucosinolates (GSL)-sulfur-containing glycosides- are the main secondary metabolites found. Their presence is evidenced whenever its tissue is disrupted, and their breakdown products are the principal responsible for the sharp and bitter-tasting flavors of these vegetables. There have been described in plant kingdom more than 120 different GSL, but in *Brassicaceae*, the amount reaches around 96, of which some are unique of some specific gender or species [20]. While genetic factors determining mainly the type of GSL, environmental factors influence the amount of them. The induction of GSL following abiotic or biotic stresses has frequently been described in order to increase the phytochemicals levels when GSL are hydrolyzed by myrosinase (thioglucoside glucohydrolase, EC 3.2.1.147) upon tissue disruption, numerous breakdown products are formed, including isothiocyanates (ITCs), thiocyanates, nitriles, ascorbigen, indoles, oxazolidine-2-thiones, and epithioalkanes depending upon different factors like pH, temperature, presence of myrosinase-interacting protein, and availability of ferrous ion [21]. Among the different GLS-degradation products formed, the most abundantly formed at physiological pH are the ITCs, which are also considered the main responsible for cruciferous foods bioactivity. Since ITCs are very unstable, their health benefits depend on numerous variables related to several factors, such as the initial GSL concentration, cooking processes, amount of vegetable intake, and human metabolism.

Because the GSL profile varies between different species and the hydrolysis conditions determine the identity and amount of ITC compounds formed, it is possible to find in the literature many ITC profiles for each species, and these profiles do not always coincide with each other. ITC profiles for each cruciferous vegetable have been extensively reviewed [22][23][24][25], and the reported information highly variable according to the extraction. It is also important to keep in mind that the majority of GLS will not always give rise to its ITC profile. For example, in radish, it has consistently been reported that the majority GLS is glucoraphasatin; however, the raphasatin levels found when the ITC profile was studied, were negligible or non-quantifiable because of the extraction conditions and the hydrolysis affecting the results, especially if the medium is polar or aqueous [26]. Furthermore, the ITC profile of each cruciferous species varies according to the cultivar or variety considered and also according to the plant tissue found [27][28]. For example, in rocket leaves, the main ITC generally detected corresponds to sativin

[29], but in rocket seeds, the main ITC detected have been erucin and sulforaphane (SFN) [30]. Accordingly, in radish seeds and sprouts, the main ITC detected was sulforaphene according to several reports [13] [27] [28] [31] (Figure 2), but in radish roots, the chief ITC have been raphasatin and sulforaphene [27] [32]. In Figure 2, a graphical example of the ITC variation inside a single plant is schematized. The foregoing demonstrates that, in order to inform the ITC profile of a cruciferous vegetable, it is very important to consider, in addition to the species, the cultivation, the plant organ under study, and the extraction and detection techniques in order to make inferences and comparisons among studies.

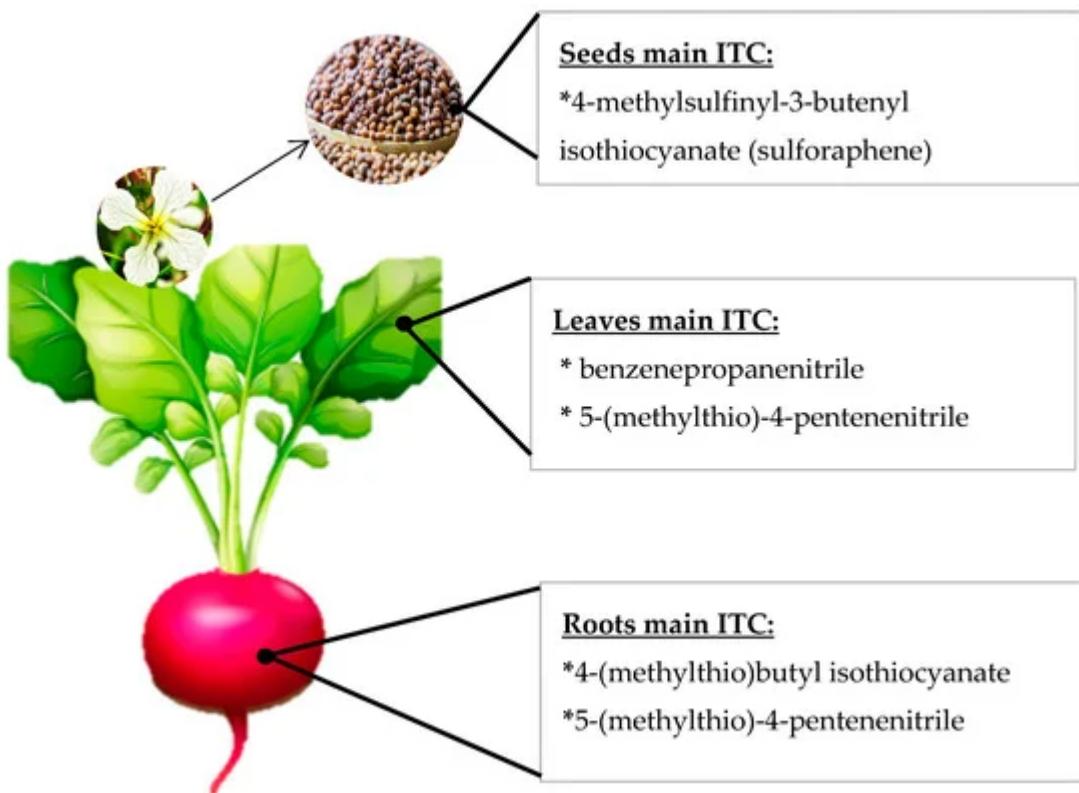


Figure 2. Schematic representation of different isothiocyanate (ITC) profiles in several radish plant organs.

3. Carotenoids

Carotenoids are highly pigmented phytochemicals that possess a C40 backbone structure and are classified as symmetrical tetraterpenes. They are produced in many plants and microorganisms, and they can be yellow, orange, or red pigments. Some carotenoids such as β -carotene and α -carotene and β -cryptoxanthin have provitamin A activity since they act as precursors of vitamin A and, therefore, acquires an important function as a human health promoter. These compounds have been extensively studied for their health-enhancing properties and also for their biological functions as attractants to pollinators, as photoprotection pigments, and as light-harvesting pigments. Similarly, to phenolic compounds, the accumulation of carotenoids in cruciferous is regulated by the environment, tissue type, and developmental stage [33] [34]. These groups of bioactive compounds have not been deeply characterized for *Brassicaceae* species, but it has been reported that the predominant ones are β -carotene and luteolin, but variable amounts of zeaxanthin, cryptoxanthin, neoxanthin, and violaxanthin have also

been detected [35][36][37]. Other reports have found that carotenoid-containing cruciferous vegetables include kale (*Brassica oleracea* L. convar. *Acephala* var. *sabellica*), brussels sprouts, broccoli, cauliflower, red cabbage, white cabbage, pakchoi (*Brassica rapa* subsp. *chinensis*), and kohlrabi (*Brassica oleracea* var. *ganglyoides*) [38][39]. Kale is considered the richest cruciferous source of this compound, surpassing cabbage in about 40 times [35]. Among these, kale stands out for its high contents, not only within the cruciferous but also when compared to other vegetables, resulting in one of the main dietary source of carotenoids [35][40][41]. Kale main carotenoids have been proposed to be zeaxanthin and luteolin [40] but important differences were found among several kale cultivars [42]. Carotenoid profile among *Brassicaceae* species varies greatly; for example, broccoli contains mainly β-carotene and luteolin [43], cabbage contains mainly luteolin, followed by β-carotene, zeaxanthin, and α-carotene [44].

4. Other Terpenes Present in *Brassicaceae* Vegetables

Other naturally occurring terpenes compounds that can be found in *Brassicaceae* vegetables are tocotrienols and tocopherols. According to Podsedeck (2007) [45], the descending order of total tocopherols and tocotrienol content in *Brassica* vegetables is as follows: broccoli > broccoli sprouts > cabbage. Furthermore, Kurilich et al. (1999) [46] reported that kale was the best source among other *Brassicaceae* vegetables of α-tocopherol and γ-tocopherol. Beside *Brassicaceae* vegetables, these compounds have also been reported in oils and cereals [47]. These phytochemicals have been extensively researched due to its anticarcinogenic properties [48][49]. Another bioactivity extensively reported in these lipid-soluble compounds is the antioxidant activity through hydrogen atom transference [50].

Phytosterols are another important terpene subclass. It has been reported to possess anti-inflammatory, anti-neoplastic, anti-pyretic, and immune-modulating activity. Also, it has been reported that phytosterols reduce serum or plasma total cholesterol and low-density lipoprotein (LDL) cholesterol [51]. Among cruciferous vegetables, *Brassica napus* L., known as rapeseed, is the most abundant natural source of phytosterols, reaching levels of up to 9.79 gr/kg oil [52]. Another rich source of phytosterols among cruciferous vegetables is *Brassica Juncea*, of which, according to the cultivar analyzed, different compositions and levels of phytosterol can be detected [53].

5. Phytoalexins

These groups of compounds were described initially in 1940 and are considered phenolic-related compounds with highly diverse chemical structures and several bioactivities, including anti-cancer properties. They possess low molecular weight and are thought to serve as an important defense mechanism for the plant [54][55]. *Brassicaceae* members containing phytoalexins present an indolic ring with C3 substitutions with N and S atoms, which confers a unique structure among other vegetables. The proposed biosynthetic pathway for phytoalexins formation includes brassinin formations from GSL; thereafter, other related phytoalexins are produced from brassinin. Klein and Sattely (2017) [55] reported that over 30 compounds arise from oxidative tailoring and rearrangement of Brassinin. Among edible cruciferous, phytoalexins have been reported in *Brassica napus* [56], *Brassica oleracea* [57], *Brassica Juncea* [58], *Sinapis alba* [59], *Wasabi japonica* [60], and in *Raphanus sativus* [61].

6. Alkaloids

Alkaloids are secondary metabolites of plants synthesized from amino acids. These nitrogen compounds have been reported in several *Brassicaceae* species, including *Capsella bursa pastoris*, *Lepidium cartilagineum*, *Nasturtium officinale*, and *Raphanus sativus*, among others [62]. Among edible *Brassicaceae* alkaloid compounds have also been reported in a cabbage cultivar collection [63], in cabbage seeds by Mohammed (2014) [64], in cauliflower leaves [65], in broccoli florets [66], and red cabbage florets [67]. Besides, a screening of tropane alkaloids—a class of alkaloids typically found in *Solanaceae* vegetables—in 43 different *Brassicaceae* species reveal that 18 of them presented alkaloid of different structures, and the authors proposed that alkaloid compounds are typical secondary cruciferous metabolites [68].

As described above, the *Brassicaceae* family is characterized by the presence of GSL and the isothiocyanates that are exclusive of this family. Also, *Brassicaceae* stands out because they possess phytochemicals of multiple chemical groups, being these species' excellent sources of bioactive compounds that have been studied throughout history. Currently, modern analytical techniques allow us to expand the knowledge about new compounds and metabolites. Consequently, it is possible to understand that each species, each *Brassica*-derived product, is themselves a mixture of multiple components. For this reason, an exhaustive determination of their phytochemical profiles must be made in each case.

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