Review Article

Perspectives of Secondary Metabolites in Reference to Vegetable Crops: A review

Abstract

Vegetables are known as protective food as they are a rich source of biologically active substances like vitamins, fibers, antioxidants, cholesterol-lowering compounds, etc. The discovery of many health-promoting compounds or nutrients was made possible through various experiments or some by chance in the past. During the time course, some novel technologies like chromatography, mass spectrometry, infrared spectrometry, and nuclear magnetic resonance came into known which enabled quantitative and qualitative measurements of a wide range of plant metabolites. Flavonoids, phenolics, and glucosinolates are the secondary metabolites that are required in plant growth & development, and stress or defence mechanism. Aside from providing strength to a plant's immune system, such metabolites influence the nutritional quality, colour, taste, and smell of the food, as well as medicinal properties. This review focused on to gather the scattered information available on the SMs which included classification, structural differentiation in between, their potential roles in defence mechanisms and ecological adaptation in reference to vegetable crops.

Keywords: Flavonoids, Nutrition, Phenolics, Phyto active compounds, Secondary metabolites

1. Introduction

Plants produce a variety of organic molecules through various metabolic pathways during the synthesis of primary metabolites (carbohydrates, fats, lipids, proteins & nucleic acids) recognized as 'secondary metabolites' (SMs) (Besancon *et al.*, 2008). SMs are low molecular weight phyto- active compounds and their synthesis is specific to tissue/organ/cell. These metabolites composed of distinct carbon skeleton structures as shown in Fig.1. SMs are not directly involved to perform any cellular functions but their presence does play a significant role in the existence of an organism in the ecosystem (Kumar *et al.*, 2022). Their level of presence & types may vary species to species, and even change within a genus. The most affecting factors that can deviate the level of SMs in the individuals are genetic, ecological and geographical factors. SMs offer plenty of protective functions against various plant stressors including abiotic stress (metal toxicity, high & low temperature, drought & flooding, salt & ionic stress, etc.), and biotic stress (insect attack, bacterial, fungal, & nematode mediated attacks, etc.). SMs have been utilized in the preparation of flavours, dyes, drugs fragrances, and can be used as insecticides too. Many positive effects on human health have been linked to these phytochemicals, including coronary heart disease, diabetes, high blood pressure, degenerative diseases, and obesity (Djoussé *et al.,* 2004). Various vegetables like broccoli, cauliflower, brussels sprouts, turnips, kale, asparagus, spinach, lettuces, and endives contain a large number of phytochemicals with antioxidant, antimutagenic, cytotoxic, antifungal, and antiviral properties (Prior & Cao, 2000; Goldberg, 2003). Significant amounts of data on the identification, biochemical characterization, localization, and health benefits of plant secondary metabolites have been accumulated over the last decade.

This review attempts to summarize the scattered information based on literature available on secondary metabolites in reference to vegetable crops, which covers the classification, nutritional value, concentration, and therapeutic uses.

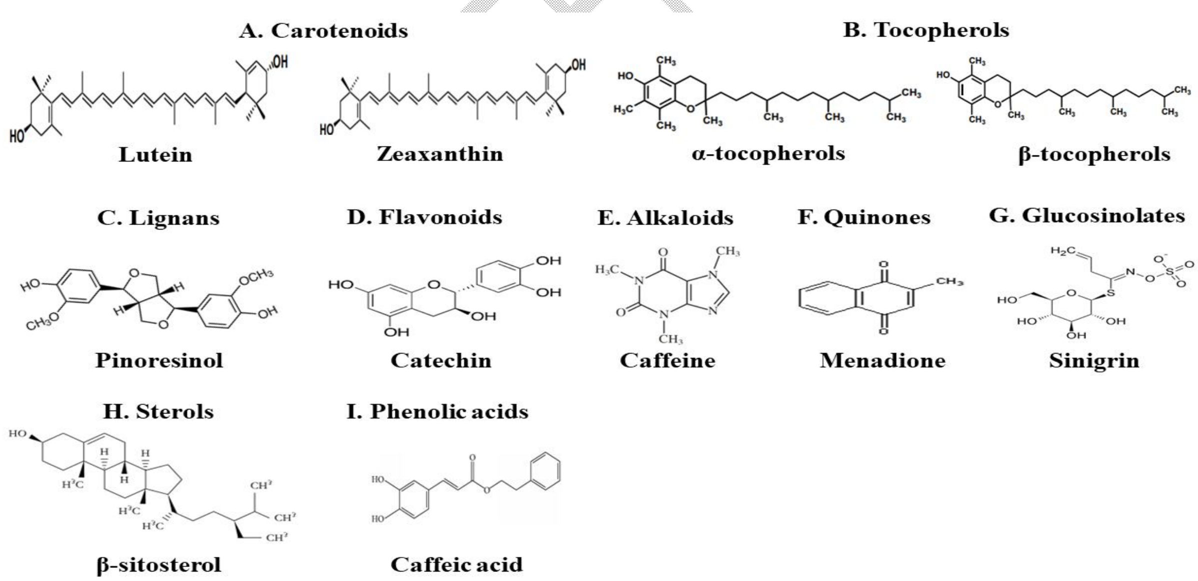

Fig. 1. Secondary metabolites featuring their unique chemical structures

2. Classification of Secondary metabolites (SMs)

The concept of secondary metabolites was first of all explained by Albrecht Kossel (1910). Later on, Czapek stated that SMs are the derivatives of nitrogen metabolism (deamination). The phytochemistry field was founded in the 20th century as a result of improvements in chroma tography techniques, which led to an increase in the recovery of these chemicals. The British nutrition foundation's nomenclature divides SMs into four major groups, namely-phenolic & polyphenolic compounds (about 8000 compounds), terpenoids (about 25000 compounds), alkaloids (about 12000 compounds), and sulfur-containing compounds (Goldberg, 2003). Different classes of SMs with their therapeutic uses have been represented in Fig. 2.

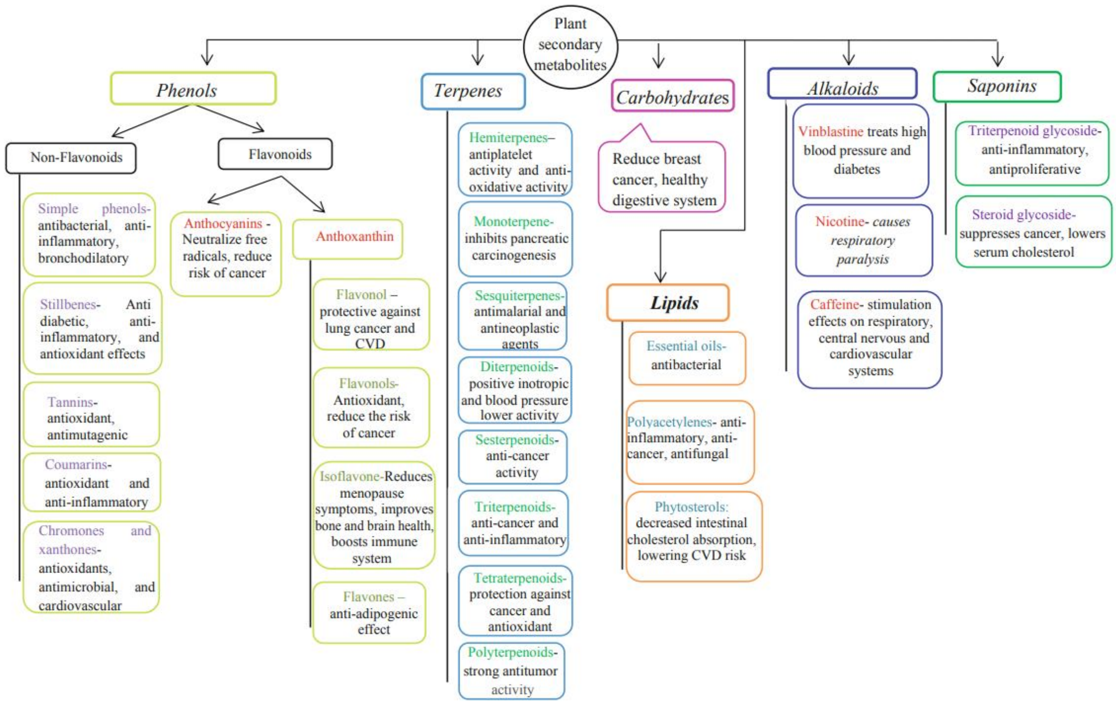

Fig. 2. Classification and therapeutic uses of SMs (Source: Kumar *et al.*, 2022)

2.1 Phenolic & polyphenolic compounds

Flavonoids, phenolic acids, and lignans are phenolic & polyphenolic compounds with aromatic or phenolic ring structures. Their high concentration provide resistance against fungal plant pathogens and protection against feeding by insects and other animals (Nicholson & Hammerschmidt, 1992). Some phenolics influence the colour pattern, fragrance, and attract the pollinators.

2.1.1 Flavonoids

This phenolic group, includes flavonols (quercetin, kaempferol, & isorhamnetin) found in onions, leeks, endives, and broccoli; flavones (apigenin, luteolin, & chrysoeriol) found in parsley, thyme, and celery; anthocyanidins (cyanidin, delphinidin, & malvidin) found in tomatoes; and isoflavones present in soy (Yao *et al.,* 2004). Many flavonoids, including anthocyanidins, chalcones, and flavones, are plant pigments that determine vegetable colour. Flavonoids in the diet have antiviral, anti-inflammatory, antihistamine, and antioxidant properties (Hou *et al.,* 2004).

2.1.2 Phenolic acids

These compounds contain at least one aromatic ring that possess one or more hydroxyl groups. Gallic and caffeic acid are found in lettuce and pak choi, while vanillic and cinnamic acid are found in onions, parsley, and spinach, and coumaric acid is found in tomatoes, carrots, and garlic (Crozier *et al.,* 2006). Caffeic, chlorogenic, sinapic, ferulic, and p-coumaric acid have high antioxidant activity due to inhibition of lipid oxidation and scavenging reactive oxygen species (Cheng *et al.,* 2007).

2.1.3 Lignans

These are diphenolic compounds that help to produce lignin, a hydrophobic component of plant cell walls. Lignans are abundant in broccoli, kale, Brussels sprouts, beans, and garlic. Lignans have several biological activities in humans, such as antioxidant and (anti) estrogenic properties, and may thus reduce the risk of certain cancers and cardiovascular diseases (Arts & Hollman, 2005). Below the Table 1 stated about the flavonoids, lignans, and carotenoids reported in vegetable crops.

Table 1. Flavonoids, lignans, and carotenoids reported in vegetable crops

Compound	Vegetable	Concentration (mg/100g FW)	Reference
Flavonoids			
Cyanidin	Red lettuce	13.7	Harnly *et al.* (2006)
Quercetin	Broccoli	3.12	(USDA)

	Endive	7.71	
	Onion	13.27	
Apigenin	Celery	4.61	(USDA)
Lignans			
Lariciresinol	Broccoli	972	Milder *et al.* (2005)
	Cauliflower	124	
	Kale	599	
	Sweet pepper	164	
Pinoresinol	Broccoli	315	
	Cabbage	568	
	Kale	1691	
Carotenoids			
α-Carotene	Carrot	4.6	(USDA)
	Peas	19	
	Sweet pepper	59	
	Tomato	112	
β-Carotene	Broccoli	779	
	Brussels sprout	450	
	Peas	485	
	Tomato	393	
β-Cryptoxanthin	Sweet pepper	2.205	
Zeaxanthin	Carrot	23	
	Kale	173	
	Lettuce	187	
	Spinach	331	
Lycopene	Tomato	3.025	

FW = fresh weight, USDA = U.S. Department of Agriculture National Nutrient Database

2.2 Terpenoids

Terpenoids are a large chemical compound family formed by the repeated fusion of branched 5-carbon isoprene units. Terpenoids play a variety of roles in plants, including membrane structural components (sterols), photosynthetic pigments (phytol, carotenoids), electron carriers (ubiquinone, plastoquinone), and hormones (gibberellins, abscisic acid) (Seiger, 1998). Carotenoids, tocopherols and tocotrienols, quinones, and sterols are examples of major dietary terpenoids.

2.2.1 Carotenoids

Plant carotenoids (α-carotenes, β-carotenes, xanthophylls, lycopene) are lipid-soluble pigments found in carrots, tomatoes, pumpkin, and sweet potatoes (Crozier *et al.,* 2006). Carotenoids in plants protect photosynthetic tissues from photooxidative damage and are precursors of the phytohormone, abscisic acid (ABA), which regulates developmental and stress processes (Taylor *et al.,* 2000). Carotenoids with provitamin A activity are required in the human diet. Vitamin A plays a role in hormone synthesis, cell growth and differentiation regulation, and immune responses. A lack of carotenoids in the human diet can cause xerophthalmia (night blindness), and death (Bender, 2003). Vegetables like kale, broccoli, brussels sprouts, cabbage, cauliflower, lettuce, asparagus, spinach, sweet potatoes, tomatoes, and turnip contain tocopherols & tocotrienols (Eitenmiller & Lee, 2004).

2.2.2 Quinones & sterols

Quinones have aromatic rings that have two ketone substitutions. Vitamin K_1 (phylloquinone) can be found in lettuce, spinach, asparagus, cabbage, kale, lettuce, cauliflower, and broccoli (Bolton-Smith *et al.,* 2000). Phylloquinone is involved in electron transport during photosynthesis as well as the generation of active oxygen species observed in response to pathogen attack or stress in plants (Lochner *et al.,* 2003). On the other side, broccoli, brussels sprouts, cauliflower, and spinach are the rich source of plant sterols (viz., sitosterol, campesterol, brassica sterol, and stigmasterol) (Piironen *et al.,* 2003). Sterols regulate the fluidity and permeability of phospholipid bilayers in plant membranes. Certain sterols are precursors of plant hormones known as brassinosteroids, which play important roles in embryonic development, cell division, plant growth, and fertility. When exposed to UV light, these sterols produce calciferol (vitamin D_2), which aids in calcium absorption and bone growth (Awad & Fink, 2000).

2.3 Alkaloids

Alkaloids are a class of basic nitrogen-containing compounds derived primarily from amino acids. Because of their distinct physiological and medicinal properties (for example, caffeine, nicotine, morphine, atropine, and quinine), alkaloids have long been of great interest. Alkaloids are typically classified according to their common molecular precursors, which include pyridine (coniine, nicotine), tropane (atropine, cocaine), isoquinone (morphine, codeine), purine (caffeine), and steroids (solanine) (Facchini, 2001). Saponins for e.g., solanine, tomatine, and chaconine are plant glucoalkaloids that have surfactant properties (Hostettmann & Marston, 2005). These can be found in a variety of crops, including peas, beans, tomatoes, spinach, asparagus, onions, garlic, and potatoes (Sparg *et al.,* 2004). Saponins have some insecticidal and molluscicide activity which protect plants from microorganisms, and have allelopathic effects on many weeds as well (Haralampidis *et al.,* 2001). Some saponins, such as sapotoxin, are toxic to humans. They can create irritation to the respiratory & digestive tract membranes, and caused urticaria (Francis *et al.,* 2002). Different alkaloids, sterols, tocopherols, quinones, and glucosinolates reported in vegetable crops are presented in the Table 2.

Table 2. Alkaloids, sterols, tocopherols, quinones, and glucosinolates reported in vegetable crops

Compound	Vegetable	Concentration	Reference
Alkaloids			
α-Tomatine	Tomato	521 to 795 µg/g FW	Kozukue *et al.* (2004)
α-Solanine	Potato	0.01 to 0.43 mg/kg FW	Sengul *et al.* (2004)
Sterols			
β-Sitosterol	Broccoli	31 mg/100 g FW	
	Brussels sprouts	34	
	Cauliflower	26	
	Celery	7.3	
	Kale	7.4	

	Tomato	2.4	
Tocopherols			
α-Tocopherol	Broccoli	1.44 mg/100g FW	Chun *et al.* (2006)
	Carrot	0.86	
	Spinach	1.96	
	Tomato	0.53	
β-Tocopherol	Carrot, Lettuce, Cucumber	0.01 mg/100g FW	
γ -Tocopherol	Broccoli	0.31 mg/100g FW	
	Cauliflower & Spinach	0.20	
	Lettuce	0.11 to 0.74	
Quinones			
Phylloquinone	Broccoli	102 µg/100 g FW	Damon *et al.* (2005)
	Celery	29	
	Cucumber	16.4	
	Lettuce	24.1 to 127	
	Sweet pepper	4.9 to 21.4	
Glucosinolates			
Sinigrin	Brussels sprouts	8.56µmol/100g FW	Song & Thornalley (2007)
	Cauliflower	5.28	
	Green cabbage	5.09	
Glucoalyssin	Broccoli	3.86 µmol/100 g FW	
Glucoraphanin	Broccoli	29.4 µmol/100 g FW	

FW = fresh weight, USDA = U.S. Department of Agriculture National Nutrient Database

2.4 Sulfur-containing compounds

Glucosinolates are a large functional group of sulfur-containing amino acid derivatives with a glucose group. Vegetables like white & red cabbage, brussels sprouts, and cauliflower contain the glucosinolates, progoitrin & sinigrin. Broccoli, red radish, and daikon contain glucoiberin & glucoraphanin. Whereas, mustard and horseradish contain sinigrin & gluconasturtiin (Johnson, 2002). Substances derived from glucosinolates act as natural pesticides and herbivore repellents. Some glucosinolates are important flavour compound precursors. Isothiocyanates like allyl isothiocyanate and benzyl isothiocyanate, also known as "mustard oils," have a pungent or lachrymatory taste and an acrid odor (Drewnowski & Gomez-Carneros, 2000). Other glucosinolates are undesirable because their breakdown products have unpleasant sensory or physiological properties. Sinigrin and its degradation product is bitter in flavour. Overconsumption of glucosinolates-rich foods can disrupt thyroid hormone synthesis and cause inflammation of the stomach mucous membranes.

2.5 Conclusion

Secondary metabolites have a well-established role in the management of general health that has contributed towards the acceptance of them as an alternative to medicines with a certain problem. Future research should be based on identifying novel SMs in vegetable crops to boost biofortification and cure various diseases. There is always a need to give emphasis on their effective distribution, stabilization, extraction, bioavailability, and other linked issues. This review would be helpful to the researchers to know about the basic concept of secondary metabolites, their classification, structural difference, potential roles in plant defence system and ecological adaptation in reference to vegetable crops.

References

Anonymous. (2005). U.S. Dept. of Agriculture Agricultural Research Service (USDA). USDA national nutrient database for standard reference release 18. Available via: http://www.nal.usda.gov/fnic/foodcomp/Data/. Accessed May 8, 2007

Arts, I. C., & Hollman, P. C. (2005). Polyphenols and disease risk in epidemiologic studies. *The American Journal of Clinical Nutrition, 81*(1), 317S-325S.

Awad, A. B., & Fink, C. S. (2000). Phytosterols as anticancer dietary components: evidence and mechanism of action. *The Journal of Nutrition, 130*(9), 2127-2130.

Bender DA. 2003. Nutritional biochemistry of the vitamins. 2nd ed. Cambridge, U.K.: *Cambridge Univ. Press*. p. 512.

Besancon, E., Guos Lok, J., Tymianski, M., & Lo, E. H. (2008). Beyond NMDA and AMPA glutamate receptors: Emerging mechanisms for ionic imbalance and death in stroke. *Trends Pharm Sci, 29*: 268-267.

Bolton-Smith, C., Price, R. J., Fenton, S. T., Harrington, D. J., & Shearer, M. J. (2000). Compilation of a provisional UK database for the phylloquinone (vitamin K1) content of foods. *British Journal of Nutrition*, *83*(4), 389-399.

Cheng, Y., Lin, C. P., Liu, H. L., Hsu, Y. Y., Lim, K. E., Hung, D., & Decety, J. (2007). Expertise modulates the perception of pain in others. *Current Biology*, *17*(19), 1708-1713.

Chun, J., Lee, J., Ye, L., Exler, J., & Eitenmiller, R. R. (2006). Tocopherol and tocotrienol contents of raw and processed fruits and vegetables in the United States diet. *Journal of Food Composition and Analysis*, *19*(2-3), 196-204.

Combs Jr, G. F., & McClung, J. P. (2016). The vitamins: fundamental aspects in nutrition and health. *Academic press*.

Crozier, A., Yokota, T., Jaganath, I. B., Marks, S., Saltmarsh, M., & Clifford, M. N. (2006). Secondary metabolites in fruits, vegetables, beverages and other plant based dietary components. *Plant secondary metabolites: Occurrence, structure and role in the human diet*, 208-302.

Croteau, R., Kutchan, T. M., & Lewis, N. G. (2000). Natural products (secondary metabolites). In: Buchanan BB, Gruissem W, Jones RL (eds) Biochemistry & molecular biology of plants. *Courier Companies, Inc.*, pp.1250-1318.

Damon, M., Zhang, N. Z., Haytowitz, D. B., & Booth, S. L. (2005). Phylloquinone (vitamin K1) content of vegetables. *Journal of Food Composition and Analysis, 18*(8), 751-758.

Djoussé, L., Arnett, D. K., Coon, H., Province, M. A., Moore, L. L., & Ellison, R. C. (2004). Fruit and vegetable consumption and LDL cholesterol: the national heart, lung, and blood institute family heart study. *The American Journal of Clinical Nutrition*, *79*(2), 213-217.

Drewnowski, A., & Gomez-Carneros, C. (2000). Bitter taste, phytonutrients, and the consumer: a review. *The American Journal of Clinical Nutrition*, *72*(6), 1424-1435.

Eitenmiller, R. R., & Lee, J. (2004). *Vitamin E: food chemistry, composition, and analysis*. *CRC Press.*

Facchini, P. J. (2001). Alkaloid biosynthesis in plants: biochemistry, cell biology, molecular regulation, and metabolic engineering applications. *Annual Review of Plant Biology*, *52*(1), 29-66.

Francis, G., Kerem, Z., Makkar, H. P., & Becker, K. (2002). The biological action of saponins in animal systems: a review. *British journal of Nutrition*, *88*(6), 587-605.

Goldberg, G. (2003). The report of a British nutrition foundation task force. *Plants: Diet and Health*, p. 347.

Haralampidis, K., Trojanowska, M., & Osbourn, A. E. (2002). Biosynthesis of triterpenoid saponins in plants. *History and Trends in Bioprocessing and Biotransformation*, 31-49.

Harnly, J. M., Doherty, R. F., Beecher, G. R., Holden, J. M., Haytowitz, D. B., Bhagwat, S., & Gebhardt, S. (2006). Flavonoid content of US fruits, vegetables, and nuts. *Journal of Agricultural and Food Chemistry*, *54*(26), 9966-9977.

Heim, K. E., Tagliaferro, A. R., & Bobilya, D. J. (2002). Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships. *The Journal of nutritional biochemistry*, *13*(10), 572-584.

Hostettmann, K., & Marston, A. (2005). Saponins. *Cambridge University*.

Hou, D. X., Fujii, M., Terahara, N., & Yoshimoto, M. (2004). Molecular mechanisms behind the chemopreventive effects of anthocyanidins. *Journal of Biomedicine and Biotechnology*, *5*, 321.

Johnson, H. E., Broadhurst, D., Goodacre, R., & Smith, A. R. (2003). Metabolic fingerprinting of salt-stressed tomatoes. *Phytochemistry*, *62*(6), 919-928.

Kozukue, N., Han, J. S., Lee, K. R., & Friedman, M. (2004). Dehydrotomatine and α-tomatine content in tomato fruits and vegetative plant tissues. *Journal of Agricultural and Food Chemistry*, *52*(7), 2079-2083.

Kumar, S., Saini, R., Suthar, P., Kumar, V., & Sharma, R. (2022). Plant secondary metabolites: Their food and therapeutic importance. Sharma, A. K., Sharma, A. (eds.), Plant Secondary Metabolites, *Springer Nature Singapore*, pp. 371-413. https://doi.org/10.1007/978-981-16-4779-6_12

Lochner, K., Döring, O., & Böttger, M. (2003). Phylloquinone, what can we learn from plants? *Biofactors*, *18*(1-4), 73-78.

Milder, I. E., Arts, I. C., van de Putte, B., Venema, D. P., & Hollman, P. C. (2005). Lignan contents of Dutch plant foods: a database including lariciresinol, pinoresinol, secoisolariciresinol and matairesinol. *British Journal of Nutrition*, *93*(3), 393-402.

Nicholson, R. L., & Hammerschmidt, R. (1992). Phenolic compounds and their role in disease resistance. *Annual Review of Phytopathology*, *30*(1), 369-389.

Prior, R. L., & Cao, G. (2000). Antioxidant phytochemicals in fruits and vegetables: diet and health implications. *HortScience*, *35*(4), 588-592.

Rice-Evans, C. A., & Packer, L. (2003). Flavonoids in health and disease. *CRC Press*.

Seiger, D. S. 1998. Plant secondary metabolism. Dordrecht, The Netherlands: *Kluwer Academic Publishers*. p. 592.

Sengul, M., Keleş, F., & Keleş, M. S. (2004). The effect of storage conditions (temperature, light, time) and variety on the glycoalkaloid content of potato tubers and sprouts. *Food Control*, *15*(4), 281-286.

Song, L., & Thornalley, P. J. (2007). Effect of storage, processing and cooking on glucosinolate content of Brassica vegetables. *Food and Chemical Toxicology*, *45*(2), 216-224.

Sparg, S., Light, M. E., & Van Staden, J. (2004). Biological activities and distribution of plant saponins. *Journal of Ethnopharmacology*, *94*(2-3), 219-243.

Sroka, Z., & Cisowski, W. H. P. S. (2003). Hydrogen peroxide scavenging, antioxidant and anti-radical activity of some phenolic acids. *Food and Chemical Toxicology*, *41*(6), 753-758.

Taylor, I. B., Burbidge, A., & Thompson, A. J. (2000). Control of abscisic acid synthesis. *Journal of Experimental Botany*, *51*(350), 1563-1574.

Yao, L. H., Jiang, Y. M., Shi, J., Tomas-Barberan, F. A., Datta, N., Singanusong, R., & Chen, S. S.
(2004). Flavonoids in food and their health benefits. *Plant Foods for Human Nutrition*, *59*, 113-122.