CHAPTER 1

Bioactive compounds from vegetable and fruit by-products

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1.1 Introduction

Consumers' contemporary eating habits are changing in consonance with 21st-century lifestyles and as a result of better understanding of the effects of food on health and quality of life. Nowadays, there is increasing demand on the part of consumers for fresh or processed fruits and vegetables, mainly as juices, canned, frozen, or minimally processed products (fresh-cut, easy-to-eat, or easy-to-prepare), among other products, that are microbiologically safe, and at the same time offering biological properties beyond nutritional factors. Numerous studies have demonstrated that phytochemicals in fruits and vegetables are the major bioactive compounds with human health benefits. Another key feature that consumers are demanding is food without synthetic additives because the synthetic molecules are suspected to cause or promote negative health effects. In line with the present tendency to consume healthy, safe foods free of synthetic additives, consumers demand natural ingredients and additives capable of not only maintaining the initial quality of food, but at the same time providing healthy properties (reducing the risk of disease) that go further than nutritional requirements.

It has been evident that the consumption of food rich in phytochemicals, as well as food enriched in them, ensures the desirable antioxidant status and helps in prevention of development degenerative diseases. Moreover, the processing of fruits and vegetables produces high amounts of by-products such as peels, seeds, stones, residual pulp, discarded whole pieces, etc., rich in phytochemical compounds (phenolic compounds, carotenoids, dietary fiber, vitamin C, minerals, etc.) that can be used as a low-cost source to obtain functional ingredients.

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1.2 Beneficial health effects obtained by consuming vegetable and fruit products rich in phytochemicals

In recent years, an increasing consumption of vegetables and fruits in the diet has been observed, due to the fact that the consumer has a greater knowledge of the beneficial properties obtained. Numerous epidemiological studies have shown a direct relationship between a diet rich in fruits and vegetables and lower incidence of degenerative diseases such as certain types of cancer, cardiovascular diseases, macular degeneration, aging, and others (Liu et al. 2000; Michels et al. 2000; Kris-Etherton et al. 2002; Trichopoulou et al. 2003; Willcox et al. 2003; Dauchet et al. 2006; Ordovás et al. 2007; Liu 2013).

This effect has been attributed to the presence of certain compounds in the food owing to determined biological activities related to health benefits known as bioactive or phytochemical compounds (Liu 2013). The biological activity of these compounds (dietary fiber, carotenoids, phenols, vitamins A, C, and E, glucosinolates, organosulphur compounds, sesquiterpenic lactones, etc.) has been studied by means of *in vitro*, *in vivo*, and human intervention studies.

In general, phytochemicals could be defined as chemical substances that can be found in vegetable products, giving them physiological properties beyond the nutritional considerations.

The beneficial mechanisms resulting from the consumption of fruits and vegetables are as yet not well known. They seem to be related to synergistic or additive interactions between the phytochemicals that could affect different pathways such as modulation of steroid hormone concentration and detoxifying enzymes; reduction of plaque aggregation and blood pressure; changes in cholesterol and hormone metabolism, antioxidant, antiviral, and antibacterial activity; stimulation of the immune response; reduction of inflammatory processes; antimutagenic and anticarcinogenic properties; and prevention and delay of cardiovascular diseases (Liu 2013; Yu and Ahmedna 2013).

It is a fact that fruits and vegetables can be processed for economical and logistical reasons in order to improve their commercial shelf-life and digestibility, in accordance with the consumer habits of each country or to facilitate the consumption by special groups (children, pregnant women, older adults, patients with certain pathologies, etc.). In addition to traditional thermal processing—such as frozen, canned, or pasteurized vegetable products, etc.—there is growing interest in the development of new processing systems that minimally modify or improve the nutritional and health properties related to the consumption of fruits and vegetables. Among these new food processing technologies, researchers, industrialists, and distributors have been focused on the development of minimal processing technologies for producing vegetable products with minimally modified sensorial and nutritional characteristics such as "fresh-cut vegetables" and "ready-to-eat processed vegetables" (González-Aguilar et al. 2005; Oms-Oliu et al. 2010; Artes and

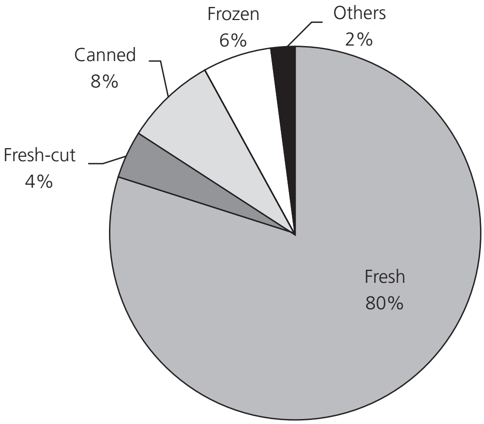


Figure 1.1 Distribution of vegetable products consumed in Europe.

Allende 2005). Figure 1.1 shows the distribution of vegetable products more frequently consumed in Europe. At present, Europeans preferably consumed fresh vegetable products (80%), and only 20% of vegetable production is consumed processed, mainly canned (8%), frozen (6%), or fresh-cut products (4%).

1.3 By-products from vegetable and fruit processing to obtain phytochemicals

There are important food mass losses throughout the supply chain that lead to edible food for human consumption. Food losses take place at the production, postharvest, and processing stages in the food supply chain. Food losses occurring at the end of the food chain (retail and final consumption) are called "food waste," which relates to retailers' and consumers' behavior (Parfitt et al. 2010). Fruit and vegetable processing generates large quantities of solid and liquid waste such us peels, seeds, stones, fruit pomace from the juice industry, and blanching liquid from the frozen vegetable industry, among others.

Figure 1.2 shows the percentage of the initial weight of fruits and vegetables that are discarded at each phase of plant food chain in different regions. It is noteworthy that in most countries, the percentage of the initial weight of vegetables and fruits that are lost or discarded is over 40%, becoming more than 50% in less industrialized countries (sub-Saharan Africa, North Africa, Central and East Asia, etc.). The losses in agricultural production between 15 and 20% dominate for industrialized regions (Europe, North America, etc.), mostly due to postharvest fruit and vegetable grading caused by quality standards set by retailers. Waste at the end of the food supply chain is also substantial, with 15–30% of purchases mass discarded by consumers (Gustavsson et al. 2011). In developing regions, losses in agricultural production dominate total losses throughout the food supply chain. Losses during postharvest and distribution stages are also

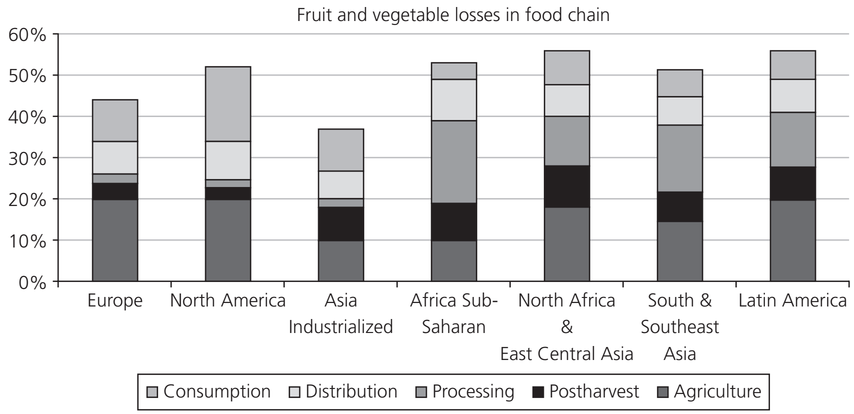


Figure 1.2 Percentage of fruit and vegetable production discarded at different phases of the plant food chain in different regions.

severe, which can be explained by deterioration of perishable crops in the warm and humid climate of many developing countries, as well as by seasonality that leads to unsaleable gluts (FAO 2011).

Every year in Europe there are more than 190 million tons of food losses and wastes from fruit and vegetable processing, which are responsible for 20–30% of the negative environmental impact that industrialized countries account for.

Discarded fruit and vegetable peels, seeds, stones, or whole pieces are considered waste if they are not used as sources of phytochemicals or other valuable products. If this waste is used for obtaining phytochemicals, then it is considered as fruit and vegetable processing by-products.

Figure 1.3 shows the flow diagram of most usual vegetable processing. This diagram shows that the first stages (1–7) are similar for the majority of processed vegetables (canned, frozen, minimally processed, etc.), and also they are the processing steps that generate the largest amount of solid by-products. Thus, in step 4, "selection and classification," whole product damaged either by mechanical injury or fungal attack is removed, and also the pieces that do not have the characteristics of size and maturity required by commercial-quality parameters are discarded. Also, in step 6, "elimination of not edible fraction," roots, leaves, pods of green peas and beans, dry outer layers of onion or garlic, outer leaves of lettuce, artichoke, or corn cobs, among others, are removed. The weight of discarded product is quite variable depending on the type of vegetable. For example, in the case of the artichoke and celery, the waste generated can be approximately 50–60% of the initial fresh weight of the vegetable, reaching 75% in the processing of peas (Larrosa et al. 2002). Finally, in step 7, "peeling and cutting," peels, seeds, and stones are discarded, generating by-products with a high phytochemical concentration (Ayala-Zavala et al. 2011).

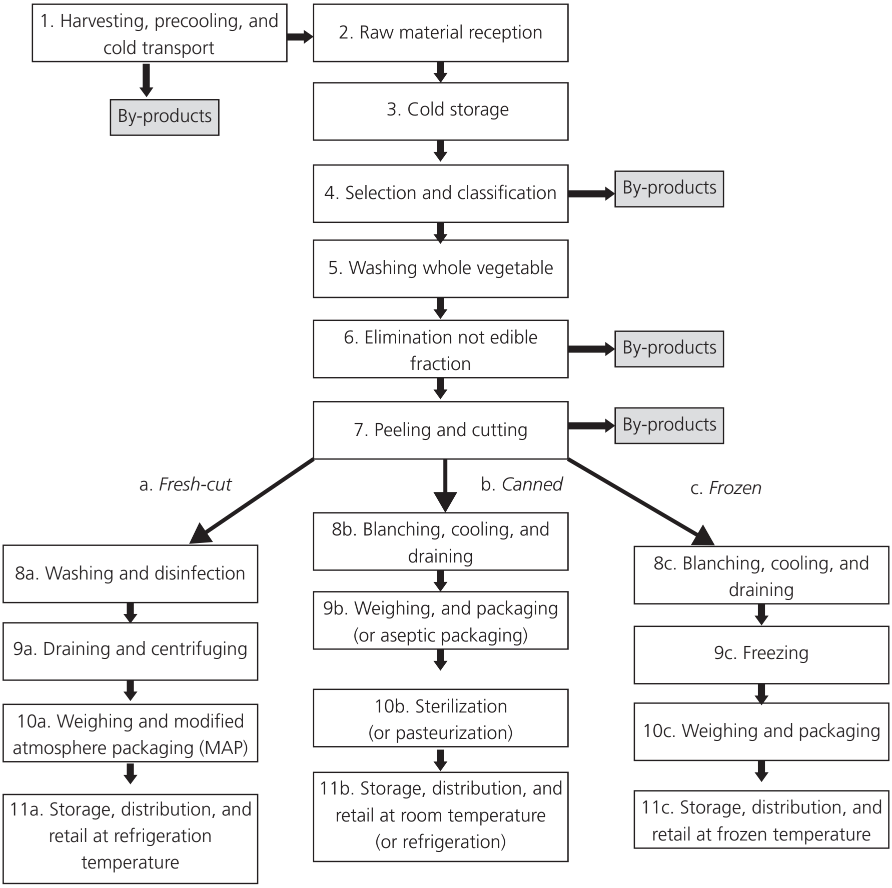


Figure 1.3 Vegetable processing flow diagram.

Fruit juices are the main processed fruit product commercialized in the whole world. Practically 40% of citrus fruit world production is processed as juices in different forms, mainly obtained from concentrate or by direct extraction, and stored at room temperature or under refrigeration (Figure 1.4). Processing of citrus fruit produced great amounts of by-products such as pulp, seeds, or fruit pomace. Figure 1.4 shows the flow diagram for obtaining juice from other types of fruits such as apples, stone fruit, grapes, or wild fruits that also produce large amounts of such by-products as peels, seeds, and stones.

From an economic point of view, the food losses produced during fruit and vegetable processing is an important problem because the cost of their management influences the final price of the product, which significantly increases due to that activity. Furthermore, disposal of this material is a serious problem as there are significant legal requirements related to its manipulation. Environmental legislation in the European Union is demanding for the treatment of waste,

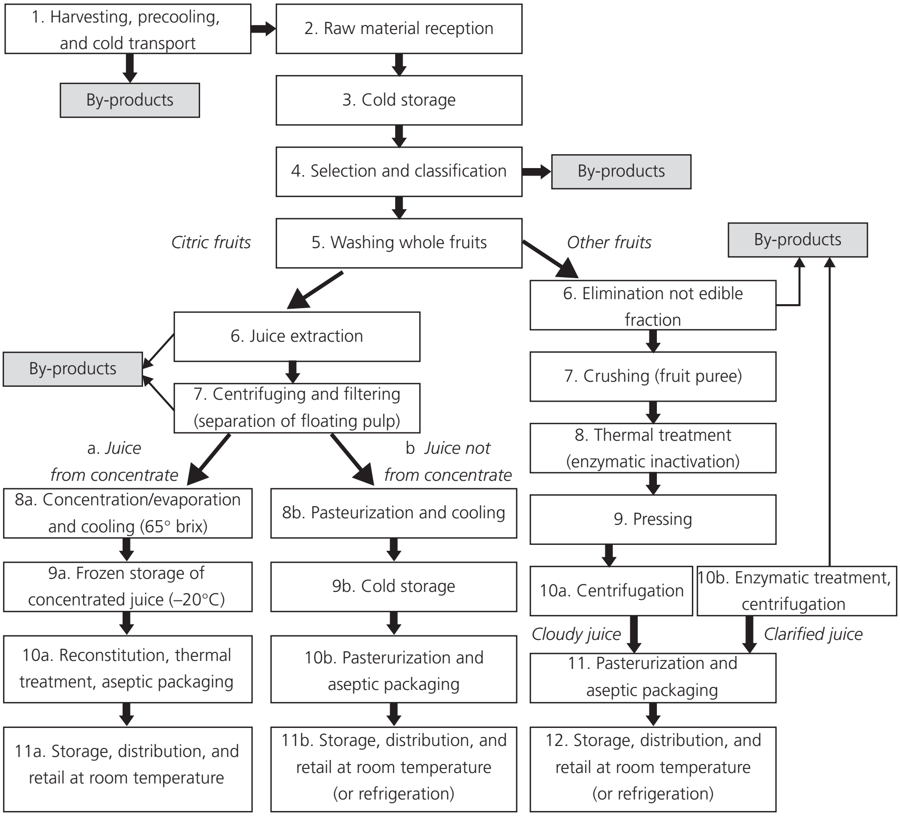


Figure 1.4 Fruit processing flow diagram.

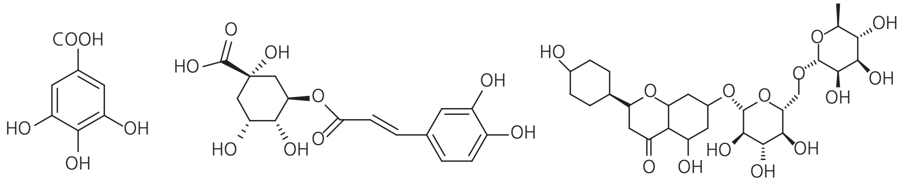
according to Directive 2006/12/EC that was subsequently improved in Directive 2008/98/EC. This Directive establishes the obligation of member states to implement measures to reduce industrial waste by recycling, recovery, and reuse as an energy source or other procedures to extract valuable raw materials.

The total or partial recovery of these wastes or by-products produced during fruit and vegetable processing or in other steps of the food supply chain involves significant advantages in economic, social, and environmental considerations. Generally, these products have been reused as animal feed, compost for farmland, or in biomass used in the production of fuels such as bioethanol (Lenucci et al. 2013).

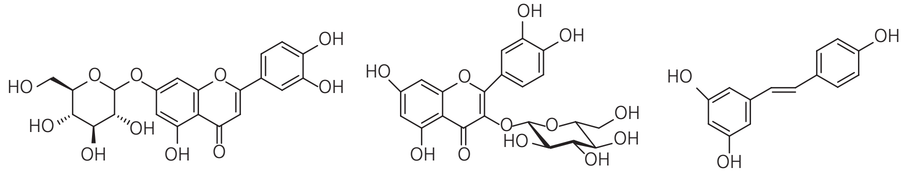
At present, producers and the food industry are looking for innovative ways of using these wastes as by-products for further exploitation on the production of additives or supplements with high nutritional and functional value. One of these innovative research lines has revealed agro-industrial by-products as a major source of phytochemicals that can be used as natural additives and functional ingredients in the formulation of new foods. Therefore, recovery and recycling of these by-products could be economically attractive to industries.

There are several reviews that summarize the published studies related to obtaining phytochemicals from agro-industrial by-products and their application in the design of new functional foods. Thus, Schieber et al. (2001) conducted one of the first reviews on the utility of fruit and vegetable processing by-products as inexpensive raw material for the production of phytochemicals with high nutritional value and potential as antioxidants (vitamin C, phenolic compounds, carotenoids, tocopherols, and minerals) (Moure et al. 2001). Since then numerous studies have been published on obtaining phytochemicals from fruit and vegetable processing by-products (Djilas et al. 2009; Aguedo et al. 2012; Kalogeropoulos et al. 2012; O'Shea et al. 2012; Wijngaard et al. 2012; Yu and Ahmedna 2013). At present, increased consumption of tropical fruits and derivatives (juices, purees, canned, fresh-cut, etc.), due to their high nutritional value and beneficial health properties, has made the processing of these fruits generate a large amount of by-products rich in phytochemicals, which can be used as natural additives with different activities (antioxidants, antibrowning, antimicrobials, colorants, texturizers, etc.) (Ayala-Zavala et al. 2011; Correia et al. 2012).

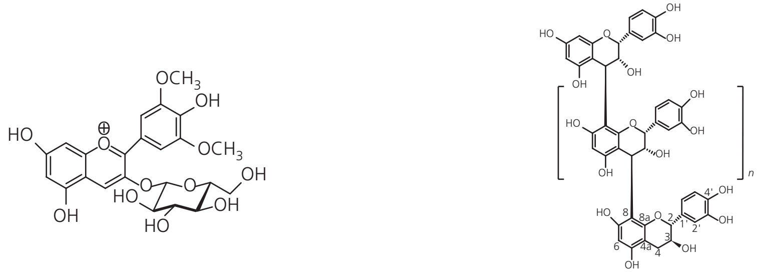
One of the major bioactive compounds obtained from agro-industrial by-products are polyphenols with antioxidant and anti-inflammatory properties (Larrosa et al. 2002; Balasundram et al. 2006; Djilas et al. 2009; Correia et al. 2012; Yu and Ahmedna 2013). Polyphenols are characterized by having at least one aromatic ring with one or more than one hydroxyl group attached. Polyphenols are generally classified into classes and subclasses based on their chemical structures (Crozier et al. 2009). Four major classes of polyphenols found in fruit and vegetable by-products are phenolic acids, flavonoids, lignans, and stilbenes. Phenolic acids are divided into hydroxybenzoic and hydroxycinnamic acids. The hydroxycinnamic acids are more common than hydroxybenzoic acids, and they mainly include gallic acid, *p*-coumaric acid, caffeic and chlorogenic acids, and also ferulic and sinapic acids. These acids are rarely found in free form and are usually extracted as glycosylated derivatives or esters of quinic acid, shikimic acid and tartaric acid. Flavonoids are the most numerous of the phenolic compounds in plant products and are divided in several subclasses: flavonols, flavones, flavan-3-ols, flavanones, anthocyanidins and isoflavones, and other minor components of the diet such as coumarins or chalcones. The main dietary flavonols, kaempferol, quercetin, isorhamnetin, and myricetin, are most commonly found as *O*-glycosides. Also flavones such as apigenin and luteolin occur as 7-*O*-glycosides. Flavan-3-ols range from the simple monomers (+)-catechin and its isomer (−)-epicatechin, which can be hydroxylated to form gallocatechins and also undergo esterification with gallic acid, to complex structures including oligomeric and polymeric proanthocyanidins, which are also known as condensed tannins. The most common anthocyanidins are pelargonidin, cyanidin, delphinidin, peonidin, petunidin, and malvidin, which are invariably found as sugar conjugates known as anthocyanins. Flavanones are present in especially high concentrations in citrus fruits. The most common



Gallic acid **Chlorogenic acid** **Narirutin**



Luteolin-7-*O*-glucoside **Quercetin-3-*O*-glucoside** **Resveratrol**



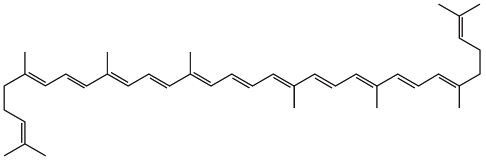
Malvidin-3-*O*-glucoside **Proanthocyanidins**

Figure 1.5 Major polyphenols found in vegetable and fruit processing by-products.

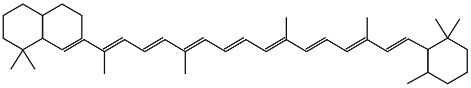
flavanone glycoside is hesperetin-7-*O*-rutinoside (hesperidin) along with narigenin-7-*O*-rutinoside (narirutin). Major stilbenoids found in foods of plant origin are resveratrol and its glucosides. Figure 1.5 shows the main polyphenols that can be extracted from fruit and vegetable processing by-products.

Carotenoids consist of a conjugated backbone composed of four isoprene units forming a C_{40} carbon skeleton. There are two general classes of carotenoids: carotenes and xanthophylls. Carotenes consist only of carbon and hydrogen atoms; beta-carotene and lycopene, mainly present in carrots and tomatoes, are the most common carotenes. Xanthophylls have one or more oxygen atoms; lutein is one of the most common xanthophylls. Lycopene is the main carotenoid that can be obtained from fruit and vegetable processing by-products (Figure 1.6).

These agro-industrial by-products also have a high content in dietary fiber with numerous beneficial physiological functions (Larrauri 1999; Garcia-Herrera et al. 2010; Aguedo et al. 2012). Soluble and insoluble dietary fiber can be extracted from fruit and vegetable by-products, the proportion between them being an important factor influencing the physiological function of this bioactive



Lycopene



Beta-carotene

Figure 1.6 Major carotenoids found in vegetable and fruit processing by-products.

compound. Thus, insoluble dietary fiber mainly acts on the intestinal tract to produce mechanical peristalsis while soluble dietary fiber can also influence available carbohydrate and lipid metabolism. O'Shea et al. (2012) summarized a large part of the studies published about the use of by-products from fruit and vegetable processing to obtain dietary fiber and other phytochemicals that may be used as functional ingredients.

In the following sections are described the main by-products obtained from the processing of vegetables and fruits used as raw material for the production of phytochemicals that can be used as functional ingredients.

1.4 Vegetable by-products

1.4.1 Lettuce (*Lettuca sativa* L.)

Lettuce (*Lactuca sativa* L.) is an annual plant of the sunflower family *Asteraceae*. It is most often grown as a leaf vegetable, but sometimes for its stem and seeds. World production of lettuce in 2011 was 24.5 million tons and China was the first producer with 13.43 million tons. It is also notable that the lettuce production in North America and Europe was 4.13 and 2.55 million tons, respectively.

Lettuce is most often used for salads, although it is also seen in other types of foods, such as in soups, sandwiches, and wraps; it can also be grilled. At present, in the context of the increasing demand from consumers for fresh-cut vegetables, lettuce salads account for 61% of all fresh-cut products commercialized in the world.

Lettuce by-products are rich in phenolic compounds. Numerous epidemiological studies have shown that a diet high in plant foods rich in phenolic compounds decreases the risk of cardiovascular disease and cancer. The beneficial health effects of the consumption of foods rich in polyphenols are associated with their antioxidant and anti-inflammatory properties. Polyphenols' properties result in the reduction of serum levels of cholesterol, triglycerides, fatty acids, and low-density lipoprotein (LDL) and the increase of high-density lipoprotein

(HDL). Furthermore, they have a high capacity to inhibit cell proliferation, favoring the reduction of cell growth rate and apoptosis. The importance of phenolic compounds in the diet is enormous. The daily consumption of phenolic compounds in the Mediterranean countries is approximately 1100 mg/day, which is 10 times higher than the intake of vitamin C and 100 times greater than β-carotene and vitamin E, although this depends on cultural habits and family traditions (Crozier et al. 2009; Mitjavila and Moreno 2012).

The phenolic composition of lettuce by-products varies with the lettuce variety as well as with the climatic conditions and agricultural practices used (frequency of irrigation, type of fertilizer, etc.). At present, there is a growing consumer demand for salads of a single variety of lettuce (Iceberg, Batavia, Trocadero, Lollo Roso, oak leaf, or romaine), or mixtures of leaves of different varieties. There is also growing consumer demand for baby leaf salads, mainly lettuce or other leafy vegetables such as spinach, chard, watercress, and rocket salad. This increase in the consumption of lettuce salads has caused the amount of lettuce by-products to rise significantly. The by-products of lettuce processing are mainly outer leaves and stems. It is worth noting that the outer leaves of lettuce have a higher content of phenolic compounds than the inner leaves (Hohl et al. 2001).

Table 1.1 shows the phenolic composition of by-products obtained from lettuce processing, shown according to the main phenolic families, variety of lettuce, and solvent used in the extraction procedure (Llorach et al. 2004).

Generally, the major phenolic fraction of lettuce is made up of caffeic acid derivatives (90%), mainly esterified with quinic acid (chlorogenic acid and isochlorogenic), tartaric acid (chicoric acid), and malic acid (Llorach et al. 2008).

Table 1.1 Phenolic compounds from lettuce and escarole by-products.

Variety (extractant)	Total Phenols (μg/g fw)	Total Flavonols (μg/g fw)	Total Flavones (μg/g fw)
Romana			
(water)	496.00	84.22	46.33
(methanol)	221.00	85.15	30.42
Iceberg			
(water)	211.05	21.84	7.14
(methanol)	108.10	24.38	9.20
Baby			
(water)	1088.00	157.70	5.80
(methanol)	1215.20	320.23	21.70
Escarole			
(water)	420.50	346.32	nd
(methanol)	415.43	407.00	nd

fw, fresh weight; nd, not detected.

Source: Llorach et al. (2004).

Flavonoid compounds in lettuce leaves represent a minor fraction (5%) of the total phenolic compounds and are mainly composed by flavonols and flavones. The most common flavonols found in lettuce are derivatives of quercetin and kaempferol conjugated with glucose and rhamnose. Flavone compounds, principally luteolin derivatives, have also been identified. Additionally, anthocyanin compounds have been identified in the pigmented leaves of lettuce, mainly derivatives of cyanidin. Frequently, the anthocyanins in red lettuce are cyanidin-3-*O*-(6-malonylglucoside) and cyanidin-3-*O*-glucoside (Llorach et al. 2008).

Thus, the majority of flavonols in lettuce are quercetin derivatives such as quercetin-3-*O*-glucoside, quercetin-rutinoside, and quercetin-glucuronide. These compounds are present at low levels in green lettuce but are more abundant in red varieties. Kaempferol derivatives were found only in escarole as kaempferol-3-*O*-glucuronide and kaempferol-3-*O*-(6-*O*-malonylglucoside). Luteolin is a flavone rarely present in green lettuces but is more abundant in pigmented lettuces such as the Lollo Roso variety, where it was found as luteolin-7-glucuronide, luteolin-7-rutinoside, and luteolin-7-glucoside.

Therefore, all phenolic compounds that have been described in lettuce are also present in the by-products resulting from its processing. Although the concentration of phenolic compounds in lettuce is relatively low, the high consumption of this product in the majority of the countries makes it one of the major sources of phenolic compounds in the human diet.

1.4.2 Tomato (*Solanum lycopersicum* L.)

Tomato is the fruit of the plant *Solanum lycopersicum* L. that belongs to the *Solanaceae* family. Tomato is consumed in many ways, either raw or as an ingredient in many dishes, sauces, purees, salads, and juices.

Tomato production is the fourth agricultural product in volume in the world after rice, wheat, and soybeans, with a production of 160 million tons (FAO 2011).

Tomatoes and processed tomato products, either sliced or in form of sauces, juices, or purees, have a high content of micronutrients (vitamin C and E, folate, and minerals), dietary fiber, and phytochemicals: phenolic compounds and mainly carotenoids such as lycopene and β-carotene (Sánchez-Moreno et al. 2008). The consumption of tomatoes and tomato products has been associated with a reduced risk of certain cancers such as prostate cancer (Giovannucci 2002). Tomato product consumption also shows a high protective effect against cardiovascular diseases due to important antioxidant and antiplatelet activities as well as reduction of blood lipid levels (George et al. 2004; Fuentes et al. 2013). Health protection associated with the consumption of processed tomato products has been highlighted by numerous *in vivo* studies. These studies have shown the reduction of certain markers of lipid oxidation and inflammation such as the oxidation of LDL cholesterol and F2-isoprostanes (Burton-Freeman et al. 2012). The protective effect of the consumption of processed tomato products has been primarily associated with the presence of lycopene

(Giovannucci 2002), highly concentrated in processed tomato products and in their by-products, mainly in the peel (Chang et al. 2006). Besides the peel, tomato processing leads to other different types of by-products such as discarded whole tomatoes, seed, and pulp. The phytochemical concentration of tomato by-products depends on different factors such as tomato variety, ripeness stage, and processing conditions. Generally, the production of juices, sauces, or tomato paste produces a solid residue consisting of 56% peels and 44% seeds (Schieber et al. 2001). The industrial yield of tomato-derived products can vary between 95 and 98% of the initial fresh weight; thus, if we consider an approximate average yield of 96%, the solid residue or by-product produced could be 4% of the raw tomato weight. It was found that tomato processing by-products—mainly peels, seeds, and pulp—have a phytochemical qualitative composition similar to the fresh tomato fruit. Generally, the peel is the by-product with the highest concentration of lycopene and phenolic compounds, while seeds also have phenolic compounds and a high content of unsaturated fatty acids, primarily linoleic acid (Schieber et al. 2001). The by-products obtained in tomato paste processing (seed plus peel) has a similar amount of total phenolic compounds and antioxidant activity, measured according to DPPH and FRAP methodologies, than the raw whole tomato. Hydroxycinnamic acids such as caffeic and chlorogenic acids predominate in raw tomato, and tomato by-products are rich in flavonoids, mainly naringenin (87%) (Kalogeropoulos et al. 2012) (Table 1.2). However, when the concentration of lycopene in the different parts of the tomato fruit was calculated in fresh

Table 1.2 Phytochemical compounds extracted from whole raw tomato and its corresponding by-product formed by peels and seeds.

Compound	Whole Raw Tomato	By-product	Significance
Carotenoids (µg/g dw)			
Lycopene	1013.2 ± 89	413.7 ± 80	**
β-Carotene	86.1 ± 4.4	149.8 ± 86	**
α-Tocopherol (µg/g dw)	85.8 ± 5.9	155.7 ± 10	**
Sterols (µg/g ps)			
β-Sitosterol	91.5 ± 2.2	378.8 ± 53	**
Stigmasterol	67.3 ± 2.5	151.7 ± 19	**
Campesterol	10.8 ± 0.8	65.6 ± 5.8	**
Polyphenols (µg/g dw)			
Hydroxycinnamic acids	105.5 ± 2.4	120.8 ± 8.3	ns
Phenolic acids	120.3 ± 2.3	128.1 ± 7.6	ns
Flavonoids	51.8 ± 2.3	378.7 ± 62	**
Naringenin (% Flavonoids)	8.3 ± 0.7	63.5 ± 4.6	**

dw, dry weight; ns, no significant.

Source: Kalogeropoulos et al. (2012).

Table 1.3 Phytochemical compounds extracted from tomato by-products.

By-product	Phytochemical	Concentration	Source
Whole	Lycopene	29 µg/g fw	Choudhari & Ananthanarayan (2007)
Peel	Lycopene	486 µg/g fw	Choudhari & Ananthanarayan (2007)
Peel (enzymatic extraction with pectinase)	Lycopene	1590 µg/g fw	Choudhari & Ananthanarayan (2007)
Whole	Lycopene	1013 µg/g dw (38.8 µg/g fw)	Kalogeropoulos et al. (2012)
Peel plus seed	Lycopene	414 µg/g dw (78.12 µg/g fw)	Kalogeropoulos et al. (2012)
Peel plus seed (solvent extraction)	Lycopene	310 µg/g dw	Baysal et al. (2000)
Peel plus seed (SFE + 5% ethanol)	Lycopene	465 µg/g dw	Baysal et al. (2000)
Peel plus seed	Lycopene	864 µg/g dw	Knoblich et al. (2005)
Peel	Lycopene	19.8 µg/g fw	Kaur et al. (2008)
Pulp	Phenols	92–270 µg/g fw	George et al. (2004)
Peel	Phenols	104–400 µg/g fw	George et al. (2004)
Pulp	Phenols	127 µg/g fw	Toor & Savage (2005)
Peel	Phenols	291 µg/g fw	Toor & Savage (2005)
Seed	Phenols	220 µg/g fw	Toor & Savage (2005)
Peel plus seed	Fiber	50% dw	Valle et al. (2006)

fw, fresh weight; dw, dry weight; SFE, supercritical fluid extraction.

weight, the tomato peel has a concentration of lycopene (486 µg/g fresh weight [fw]) significantly greater than the whole tomato (29 ug/g fw) (Choudhari and Ananthanarayan 2007) (Table 1.3). The use of enzymes capable of hydrolyzing the cell walls such as cellulases and pectinases can increase by 107% and 206%, respectively, the extraction of lycopene from tomato peels (Choudhari and Ananthanarayan 2007) (Table 1.3). In addition, extraction systems using supercritical extraction with carbon dioxide in the presence of ethanol may increase up to 50% the quantity of lycopene extracted from tomato peels (of 309–465 µg/g dry weight) (Baysal et al. 2000).

In addition to lycopene, tomato-derived products are also rich in phenolic compounds, having shown that tomato peel and seeds have a higher concentration of phenolic compounds than pulp (Table 1.3) (Kalogeropoulos et al. 2012).

The phytochemical composition of the by-products obtained from vegetable processing makes them valuable sources of nutritional ingredients for obtaining a great variety of functional foods. Table 1.4 shows some examples of functional foods obtained from tomato by-products.

Table 1.4 Foods functionalized with ingredients obtained from vegetable processing by-products.

Vegetable	By-product	Phytochemical	Food	Functionalization	Source
Tomato	Peel (powder)	Lycopene	Burger	Increase lycopene level	García et al. (2009)
	Tomato pulp	Lycopene Fiber Fenoles	Ketchup	Natural thickener	Farahnaky et al. (2008)
	Peel (powder)	Lycopene β-carotene	Sausage	Increase carotenoid level	Calvo et al. (2008)
Onion	Peel plus outer coats	Phenols	Tomato juice	Increase phenol level	Larrosa et al. (2002)
Carrot	Crownes plus tips	Phenols	Tomato juice	Increase phenol level	Larrosa et al. (2002)
	Waste	Phenols	Beverages	Increase phenol level	Stoll et al. (2003)
	Waste	Phenols	Honey candy	Increase shelf-life to 6 months at 30°C	Durrani et al. (2011)
Artichoke	Outer leaves or blanching liqueur	Phenols	Tomato juice	Increase phenol level	Larrosa et al. (2002)
Potato	Peel	Fiber	Wheat bread	Increase fiber level	Kaack et al. (2006)

1.4.3 Artichoke (*Cynara scolymus* L.)

Artichoke (*Cynara scolymus* L.) is a flowering plant cultivated as food that belongs to the *Asteraceae* family, native to the Mediterranean area. World production of artichokes in 2011 was 1.5 million tons, and the Mediterranean countries were the major producers: Italy (474.550 tons), Egypt (202.458 tons), and Spain (182.120 tons) (FAO 2011).

Artichoke processing discards approximately 50–60% of the initial fresh weight as a by-product mainly formed by outer leaves and part of the stem. These by-products are very rich in phenolic compounds. Furthermore, some processing technologies require previous blanching to inactivate spoilage enzymes (polyphenoloxidase, peroxidase, etc.). This pre-treatment results in a high amount of solid and liquid (water blanching) wastes with a high concentration of valuable phenolic compounds and dietary fiber (Table 1.5) (Femenia et al. 1998; Larrosa et al. 2002).

Consumption of artichoke or derived products has been shown to produce health benefits, especially hepatoprotective, anticancer, and hypocholesterolemic effects (Llorach et al. 2002). Artichoke consumption has also significant antioxidant properties due to its high content in caffeic acid derivatives such as

Table 1.5 Phytochemicals extracted from artichoke by-products.

Vegetable	By-product	Phytochemical	Concentration*
Artichoke	Blanching leaves	Phenols	4320 μg/g fw
	Blanching liqueur	Phenols	6380 μg/mL
	Blanching leaves	Phenols	4400 μg/g fw
	Blanching liqueur	Phenols	6600 μg/mL

*Chlorogenic acid equivalents; fw, fresh weight.
Source: Larrosa et al. (2002).

chlorogenic acid (5-*O*-caffeoylquinic). This vegetal also presents a high content in flavonoids, especially glucosides and rutinosides, derivatives of apigenin and luteolin, and derivatives of cyanidin-caffeoylglucoside. Therefore, solid and liquid by-products from artichoke processing are an important source of phenolic compounds with antioxidant properties and a protective effect on health. However, due to the heat treatment applied to the artichoke, some phenolic compounds are converted into their isomers. Thus, the cynarin (1,3-*O*-dicaffeoylquinic acid) and neochlorogenic acid (3-*O*-caffeoylquinic acid) found in artichoke-derived products come from the isomerization of 1,5-*O*-dicaffeoylquinic acid and chlorogenic acid, respectively. Despite such phenolic isomerization, artichoke by-products have a high antioxidant capacity that makes them very useful as functional ingredients (Llorach et al. 2002). Table 1.4 shows examples of functional foods obtained by using artichoke by-products.

1.4.4 Carrot (*Daucus carota* L.)

Carrot (*Daucus carota* L.) is a root vegetable that belongs to the *Apiaceae* family. This plant is known for its characteristic orange color, although there are also some purple, red, yellow, and white varieties. World production of carrots in 2011 was 35.66 million tons and more than half were grown in China (FAO 2011).

Carrot is a root vegetable that is mostly consumed in the Mediterranean diet (fresh, frozen, canned, dehydrated, etc.). Nowadays carrots are extensively commercialized as a fresh-cut product or minimally processed vegetable as mini carrots or strips and sticks that have been peeled, washed, sliced, or diced. Carrots are used in a variety of ways—in salads and soups, for example. Also, it is one of the principal components of purees destined for baby food and healthy beverages combined with other vegetables.

Carrot processing produces different types of by-products: whole pieces eliminated due to defects, crowns and root tips, and peelings. Thus, by-products from carrot processing may have a phytochemical composition qualitatively similar to those of the whole carrot that usually depends on the variety, cultivation conditions (irrigation, fertilizer, etc.), and processing conditions. Carrot gets its characteristic bright orange color from β-carotene, and lesser amounts of α-carotene

Table 1.6 Phytochemicals extracted from different carrot varieties.

Color variety	Total phenols (mg GAE/g fw)*	Chlorogenic acid (μg/g dw)	Total carotenoids (μg/g dw)	β-carotene (μg/g dw)	α-carotene (μg/g dw)	Lycopene (μg/g dw)
Purple-orange	38.7 ± 5.4a	18790 ± 38a	771.0 ± 22e	128 ± 17d	18.9 ± 2c	3.68 ± 2.03b
Purple-yellow	15.0 ± 1.1b	7661 ± 4.9b	334.2 ± 12d	239 ± 8c	83.7 ± 4c	2.02 ± 0.28b
Red	2.27 ± 0.1c	1347 ± 2.3c	610.1 ± 40c	187 ± 18c	1.74 ± 0.7c	419.4 ± 49a
Dark orange	1.66 ± 0.1c	631 ± 0.56c	1334.7 ± 71a	940 ± 54a	382 ± 18a	7.76 ± 0.89b
Orange	2.34 ± 0.05c	1150 ± 0.30c	816.3 ± 17b	579 ± 79b	228 ± 141b	5.09 ± 1.52b
Yellow	1.97 ± 0.6c	306 ± 1.59c	52.0 ± 17f	30 ± 8e	1.86 ± 1.2c	0.32 ± 0.10b
White	2.35 ± 0.32c	978 ± 2.78c	17.6 ± 11f	2.8 ± 4e	0.5 ± 0.33c	0.35 ± 0.0

*GAE, gallic acid equivalents; fw, fresh weight; dw, dry weight.
Different letters in the same column indicate significant differences ($p < 0.05$).
Source: Sun et al. (2009).

and γ-carotene. α- and β-carotenes are partly converted into vitamin A in humans. Carrot processing by-products present different types of phytochemicals, mainly carotenoids, but also phenolic compounds. The concentration of these phytochemicals varies depending on the variety and the process employed, as shown in Table 1.6. All carrot varieties have a very high concentration of chlorogenic and caffeic acids derivatives, including 3-*O*- and 5-*O*-caffeoylquinic acid, 3-*O*-*p*-cumorylquinic and 5-*O*-feruoylquinic acid, and 3,5-dicaffeoylquinic acid. Derived compounds from *p*-hydroxybenzoic and ferulic acids have also been identified.

It is noteworthy that purple carrot varieties have a higher total phenolic concentration than the other varieties (Table 1.6), with 5-*O*-caffeoylquinic acid (540 μg/g dw) concentration 10 times higher than other varieties. Moreover, purple carrot varieties showed anthocyanins in their phenolic composition and also higher antioxidant capacity (DPPH and ABTS) than other varieties (Sun et al. 2009). Furthermore, orange carrot varieties have higher concentrations of total carotenes (lutein plus α-carotene plus lycopene plus β-carotene) than other varieties.

Generally, β- and α-carotene are the major carotenoids in orange carrots, ranging between 13–40% and 44–79% of the total, respectively, while lycopene is the principal carotenoid (419 μg/g dw) in red varieties (Table 1.6) (Sun et al. 2009).

The solid residue obtained from carrot processing also has high dietary fiber content. Thus, 63.6% of the dry weight of the solid residue is composed of total fiber, soluble fiber being 50% of the total (Chau et al. 2004).

This solid residue also contains high concentrations of phytochemicals mainly phenolic and carotenoid compounds that can be used to obtain functional ingredients with antioxidant properties. It is also significant that solid carrot by-products have the advantage of not transferring undesirable flavors to the food to which it is added (O'Shea et al. 2012). Table 1.4 shows some examples of functional food obtained by adding carrot by-products.

1.4.5 Onion (*Allium cepa* L.)

Onion (*Allium cepa* L.) is the bulb of the onion plant and the vegetable most widely cultivated of the genus *Allium* that belongs to the *Liliaceae* family. World onion production in 2011 was 86 million tons. Onion is cultivated and used around the world and it is an important vegetable of the Mediterranean diet. Onions can be found as fresh, frozen, canned, caramelized, dehydrated, pickled, and chopped, and also as fresh-cut products. Onion is often chopped and consumed fresh in salads, or cooked and fried as part of many dishes. Onion varieties of many different colors are known: yellow, brown, red, purple, and white. Onion by-products are mainly made up of the outer peel, the next two layers, the top and bottom of the bulb, the roots, and whole pieces discarded because of mechanical damage, microbial contamination, or deformation (Benítez et al. 2012). This waste cannot be used neither for animal feed due to its strong aroma nor as fertilizer because it decomposes quickly due to the growth of plant pathogens (*Sclerotium cepivorum*). Its destruction by incineration presents serious inconveniences due to air pollution and high economical cost because of its large water content. Therefore, researchers and producers are investigating new and more advantageous systems for reusing these by-products as a source of functional ingredients. Thus, these residues can be used to obtain functional ingredients as the onion has in its chemical composition numerous biologically active phytochemicals. The beneficial health effects resulting from onion intake have been linked to their antioxidant, anti-inflammatory, and antimicrobial properties, among others (Griffiths et al. 2002; González-Peña et al. 2013). In fact, onion consumption has been associated with a significant reduction in the risk of cardiovascular disease and certain types of cancer (Hertog et al. 1993; Roldán-Marín et al. 2009a, 2010).

The beneficial health effects of onion have been linked to the high concentration of bioactive compounds such as flavonoids, sulphur compounds like sulphoxides of *S*-alk(en)yl-L-cysteine (ACSOs), fructooligosaccharides such as inulin, and dietary fiber (Griffiths et al. 2002; Benitez et al. 2012; González-Peña et al. 2013; Colina-Coca et al. 2013, 2014). Onion is one of the major sources of dietary flavonoids in Europe, containing mainly two subclasses of this polyphenolic group: anthocyanins, responsible for the purple-red of some varieties, and flavanols such as quercetin and its derivatives, which are responsible for the yellowing of the pulp and the brown skin of other varieties.

It is noteworthy that flavonols, mainly quercetin derivatives, are in a much higher concentration (280–400 mg/kg) in the onion when compared with other vegetables (100 mg/kg in broccoli, 50 mg/kg in apple, or 30 mg/kg in tea). It is also noted that the concentration of flavonols in the outer skin of onions is higher than in the other parts of the onion, especially in brown-colored ones (Benítez et al. 2011). The most abundant flavonols in this vegetable are derivatives of quercetin, mainly quercetin-4′-*O*-glycoside and quercetin-3,4′-*O*-diglucoside, in addition to small quantities of isorhamnetin-4′-glycoside and other quercetin glycosides (González-Peña et al. 2013). Moreover, some onion varieties have other quercetin, kaempferol, and isorhamnetin glycosides, and also anthocyanins. Thus, red onions, besides having a composition rich in flavonols as yellow onions, have a high concentration of anthocyanins (250 mg/kg), consisting mainly of cyanidin-3-*O*-(6′-malonylglucoside). Therefore, by-products formed by the brown external peel, the first flesh layer, and the top cut and the bottom of the bulb may be used as sources of functional ingredients because they are very rich in dietary fiber (insoluble fraction) and flavonols (quercetin derivatives), demonstrating an important antioxidant, anti-inflammatory, and protective properties against cardiovascular disease. Numerous studies have shown that the brown outer peel has the highest concentration of quercetin such as aglycone and calcium, and the top and bottom parts of the bulb have the highest concentration of minerals. Therefore, outer onion layers rich in these compounds can be used as raw material for obtaining flavonols and dietary fiber, while the inner layers are better sources of fructans and sulphoxides of *S*-alk(en)yl-L-cysteine. As an example of the high concentration of phytochemicals presented in onion by-products, Table 1.7 shows the composition of onion cv. Recas and its by-products (Benítez et al. 2011). Numerous published studies have investigated the potential of such by-products as raw materials for the production of bioactive ingredients (Roldán-Marín et al. 2009a, 2009b, 2010; Benítez et al. 2011;

Table 1.7 Phytochemical from whole onion cv. Recas and its by-products.

	Total phenols (mg GAE/g dw)[1]	**Total flavonoids (mg/g dw)[2]**	**Total ACSOs (μmol/g dw)**	**Total dietary fiber (mg/g dw)**	**AA (FRAP) (μmol Fe^{2+}/g dw)[3]**
Whole onion	17.3 ± 1.3	10.3 ± 0.3	23.8	291	83.5 ± 1.8
Brown outer peel	52.7 ± 0.9	43.1 ± 41.8	4.6	750	227.8 ± 3.2
Outer flesh layers	19.7 ± 1.6	19.5 ± 0.7	29.9	312	105.1 ± 0.6
Inner flesh layers	9.4 ± 0.6	7.0 ± 0.1	54.2	222	28.7 ± 1.7
Upper and lower cut	30.5 ± 2.0	25.9 ± 0.7	22.2	667	156.1 ± 1.6

[1] GAE, gallic acid equivalents; [2] Quercetin equivalents; dw, dry weight; ACSOs, *S*-alk(en)yl-L-cysteine sulphoxides; [3] AA, antioxidant activity.
Source: Benítez et al. (2011).

González-Peña et al. 2013; Colina-Coca et al. 2013, 2014). Table 1.4 shows an example of functional food obtained by adding onion by-products.

1.4.6 Potato (*Solanum tuberosum* L.)

Potato is a starchy, tuberous crop than belongs to the *Solanaceae* family. The word *potato* may refer to the plant itself, in addition to the edible tuber. The world production of potatoes in 2011 was about 373 million tons. China is the largest producer of potatoes in the world, and almost one-third of the world's production is harvested in China and India (88.4 and 42.3 million tons) (FAO 2011).

Potatoes can be prepared in many ways: whole or peeled, cut up, with seasoning or without. Generally, the potato has to be peeled and cut before being processed for consumption with the aim of swelling the starch granules (boiled, steamed, baked, grilled, fried, dehydrated, etc.). Most common potato dishes consist of boiled potatoes (served hot or cold in salads), mashed potatoes, or fried potatoes as chips.

Peeled and sliced potato generates many by-products each year, which are made up mainly of peels. These by-products have a high content of dietary fiber, carbohydrates, starch, and phenolic compounds whose concentrations vary depending on the potato variety (Table 1.8). Whole potato fiber content with peel (2 g) is equivalent to that of many whole-grain breads, pastas, and cereals. In general, potato contains vitamins and minerals, as well as different phytochemicals, such as carotenoids and natural phenols. Phenolic compounds in potatoes are mostly in soluble form (free phenols, soluble esters, and glycosides)

Table 1.8 Phenolic compounds from whole potatoes and their corresponding by-products.

Potato variety Product	Chlorogenic acid (μg/g fw)*	Total phenols (μg/g fw)
Van Gogh		
Whole-boiled-peeled	41 ± 2	100
Fresh peel	260 ± 25	340
Boiled peel	230 ± 0.3	440
Rosamunda		
Whole-boiled-peeled	8.6 ± 1.5	19
Fresh peel	150 ± 11	250
Boiled peel	130 ± 2.3	230
Nicola		
Whole-boiled-peeled	91 ± 2.8	170
Fresh peel	230 ± 15	350
Boiled peel	270 ± 11	450

*Caffeic acid quivalents; fw, fresh weight.

Source: Mattila and Hellström (2007).

and to a lesser degree in the insoluble form due to the phenols attached to the cell wall. Ninety percent of potato phenolic compounds in soluble form in the pulp and skin are hydroxycinnamic acid derivatives, fundamentally chlorogenic acid derivatives. Other phenolics found in potatoes are 4-*O*-caffeoylquinic acid (crypto-chlorogenic acid), 5-*O*-caffeoylquinic (neo-chlorogenic) acid, and 3,4-dicaffeoylquinic and 3,5-dicaffeoylquinic acids. The purple-colored varieties have a higher content of anthocyanins and flavonoids than the white-fleshed varieties. It is noteworthy that the peel and the adjacent flesh have phenolic compound concentration and antioxidant activity up to 50% higher than the rest of the pulp (Albishi et al. 2013). The main soluble phenolic compound in potato peel is chlorogenic acid and its derivatives (Mattila and Hellström 2007).

Phenolic compound concentration in boiled potato peel varies from 230 to 450 µg/g fw. This concentration was significantly higher than that found in boiled whole potato (100–170 µg/g fw) (Table 1.8). Thus, by-products of the processing of potatoes, constituted mainly by peels, are excellent raw materials for obtaining functional ingredients (Mattila and Hellström 2007) (Table 1.8). There are numerous published studies that found strong correlations between the intake of foods rich in phenolic compounds such as chlorogenic acid and antioxidant and anti-inflammatory properties as well as beneficial health effects such as antitumor properties and glycemic index reduction. Therefore, a natural ingredient derived from potato peels would be suitable for consumers with diabetes (O’Shea et al. 2012). Table 1.4 shows an example of low-glycemic bread obtained by adding a powder by-product from potato peels.

1.4.7 Beet (*Beta vulgaris* L.)

Consumption of leaves (*Beta vulgaris* L. var. *cycla*) and beetroot (*Beta vulgaris* L. var. *rubra*) is common in the Mediterranean diet and are increasingly used as an ingredient in salads or cooked dishes worldwide. The main producers are the Russian Federation (47.64 million tons), France (38.10 million tons), and the United States (26.21 million tons).

By-products of sugar beet processing are mainly composed of leaves, crowns, and outer layers of the root and pulp. Traditionally, beet by-products have been reused in animal feed for the production of fertilizers, natural bio-absorbent for the pretreatment of wastewater, or for obtaining alcohols and biofuels. However, these by-products are an important source of biologically active compounds such as fiber, betaine, betalains, polyphenols, minerals, etc., which have a significant value as functional ingredients (Pyo et al. 2004; Stintzing and Carle 2007; Canadanovic-Brunet et al. 2011; Ninfali and Angelino 2013).

Beet roots have nitrogen-soluble pigments known as betalains, which consist primarily of two types of compounds: red pigments called betacyanins, betanin being the majority, and the yellow pigments or betaxantinas such as vulgaxanthin. It is estimated that the average concentration of betalains in red beet root is 1.2 g/kg fw. In fact, there is a commercial natural food coloring called “red beet”

Table 1.9 Phytochemicals extracted from different beet varieties.

Variety	Plant area	Total phenols (mg/g dw)	Total flavonoids (mg/g dw)	ORAC (μmolTE/g dw)
Beta vulgaris var. *cicla*				
	Leaves	11.12 ± 0.56	7.92 ± 0.39	192.8 ± 9.6
	Roots	0.72 ± 0.04	0.88 ± 0.05	8.54 ± 0.43
	Seeds	1.88 ± 0.76	1.55 ± 0.08	49.10 ± 2.76
Beta vulgaris var. *rubra*				
	Leaves	12.76 ± 0.76	11.64 ± 0.81	200.3 ± 11.2
	Roots	1.77 ± 0.08	1.44 ± 0.15	18.21 ± 0.86

dw, dry weight.
Source: Ninfali and Angelino (2013).

(E162), consisting mainly of betanin obtained from beet root. The industrial yield of this coloring is 0.5 g of betanins per kilogram of beet root (Stintzing and Carle 2007). Beets and their by-products are also a good source of dietary fiber, vitamin C, and minerals such as potassium, manganese, zinc, copper, iron, and folic acid. Beet by-products have a high concentration of nitrates. The concentration of phenolic compounds is also important in beets, with a greater concentration of total phenols, total flavonoids, and antioxidant capacity values (measured by ORAC methodology) in leaves than in roots (Table 1.9) (Ninfali and Angelino 2013). The major phenolic compounds described in the leaves of red beet (var. *cycla*) are syringic acid (44 mg/100 g), followed by caffeic acid (15 mg/100 g) and coumaric acid (11 mg/100 g). Also ferulic acid, vanillic acid, protocatechuic acid, *p*-hydroxybenzoic acid, chlorogenic acid, and the flavonoid kaempferol are found in red beet leaves (Pyo et al. 2004). The leaves and seeds of beet (var. *cycla*) have a high concentration of a flavonoid derived from apigenin called vitexin, whose anticancer properties are widely recognized (Ninfali and Angelino 2013).

Beet products (juices, dried powder) and its by-products have been used in traditional medicine for thousands of years. The beneficial effects of the consumption of derivatives of red beet root are largely related to the presence of the betalains, which have antioxidant (free radical scavenger), anti-inflammatory, antitumor, and hypoglycemic properties. It is important to highlight their protective effect against cardiovascular disease by reducing blood pressure, platelet aggregation and lipid levels, and blood cholesterol. It also has protective properties of liver cells (Kanner et al. 2001; Ninfali and Angelino 2013). Beetroot has an N-methylated amino acid called trimethylglycine (N, N, N-trimethylglycine) or betaine. Its concentration in sugar beet root is relatively high, 1.0–1.5% on a dry solid basis. The dry residue from the processing of beet normally contains a range between 3 and 8% of betaine. Its main physiological functions are to protect cells under stress (osmoprotectant effect), while serving as a source of methyl groups necessary for the formation of many biochemical pathways.

Historically, we have used betaine supplementation to control excess blood homocysteine (caused by a hereditary condition known as homocystinuria) and reduce heart disease, stroke, cancer, and Alzheimer disease risk (Sacan and Yanardag 2010).

Therefore, beet processing by-products may also be considered in the design of functional foods as raw materials suitable for obtaining biologically active natural ingredients.

1.5 Fruit by-products

1.5.1 Fruits

Citrus is one of the most important fruit crops worldwide, with a production in 2011 of 131.20 million tons, China being the first producer with 29.99 million tons followed by Brazil (22.01 million tons) and the United States (10.70 million tons). There is also remarkable production in Mediterranean countries such as Spain (5.77 million tons), Italy (3.84 million tons), and Egypt (3.73 million tons) (FAO 2011).

The main use of citrus in food industries includes fresh juice (mainly orange juices) and citrus-based beverages. Practically 40% of citrus fruit production goes to the production of juices. During the production of citrus juices, approximately 50–60% of fresh fruit weight account as by-product. These large amounts of processed citrus fruits result in very large amounts of by-products. The main citrus processing by-products are whole fruit discarded in the selection process, peel, pulp, and seeds. The citrus peel is the main by-product, which represents 50% of fresh fruit weight. Citrus peel is traditionally dried and used in animal feed. Nowadays, citrus peel is an important source of valuable products such as volatile flavoring compounds, used in the cosmetic and perfume industries, phenolic and carotenoid compounds, and phytochemicals such as limonoids, oxygenated terpenoids (Djilas et al. 2009; Lagha-Benamrouche and Madani 2013). Also, citrus peel is an important source of fiber since it is very rich in pectins (Rodríguez et al. 2006). The pulp, separately in different steps of citrus juice production, represents 5% of fresh fruit weight and is a valuable by-product for the recuperation of phenolic and carotenoid compounds. Citrus seeds represented only 0–1.5% of fresh fruit weight, depending on the variety, and can be used for the extraction and recuperation of terpenoids.

In general, citrus peels have higher concentrations of dietary fiber and phenolic compounds than their corresponding peeled fruit. Thus, Figure 1.7 shows that the contents of total soluble and insoluble dietary fiber in peels of several citrus fruits were significantly higher than in the peeled fruit. Regarding phenolic compounds, Table 1.10 shows that the total phenolic content in the peels of oranges, lemons, and grapefruit was approximately 15% higher than those found in the peeled fruits (Gorinstein et al. 2001). Like the total phenol content,

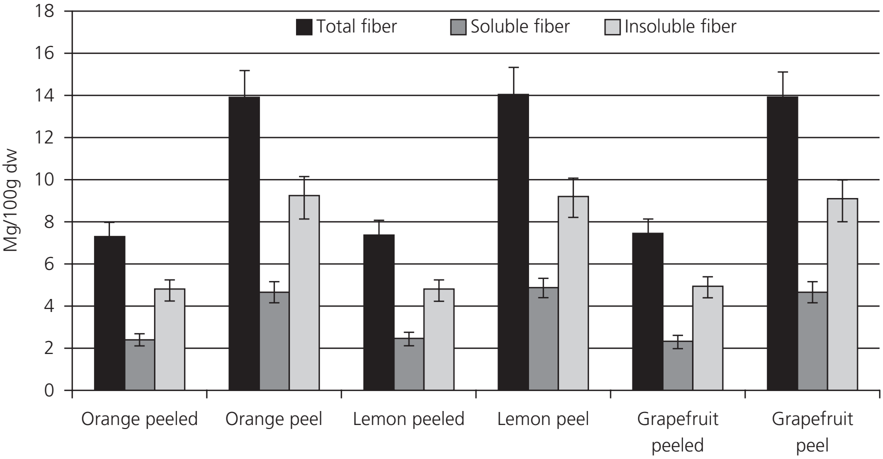


Figure 1.7 Total soluble and insoluble fiber content in peel and pulp of citrus fruits.

Table 1.10 Total phenolic content, phenolic acids, and antioxidant activity in citrus peel and their peeled fruit.

Variety	Total phenols*	Ferulic acid*	Sinapic acid*	*p*-Cumaric acid*	Caffeic acid*	TRAP** (nmol/ml)
Orange peeled	154 ± 10.2	34.1 ± 3.1	30.71 ± 3.1	24.10 ± 2.2	8.10 ± 0.8	2111 ± 199
Orange peel	179 ± 10.5	39.2 ± 4.0	34.90 ± 3.1	27.90 ± 2.5	9.50 ± 0.8	3183 ± 311
Lemon peeled	164 ± 10.3	38.8 ± 4.1	36.40 ± 3.1	31.30 ± 3.1	12.10 ± 0.8	4480 ± 398
Lemon peel	190 ± 10.6	44.9 ± 4.2	42.10 ± 4.1	34.90 ± 3.4	14.20 ± 1.3	6720 ± 601
Grapefruit peeled	135 ± 10.1	27.1 ± 3.0	27.30 ± 2.9	10.80 ± 1.1	5.0 ± 0.5	1111 ± 102
Grapefruit peel	155 ± 10.3	32.3 ± 3.1	31.90 ± 3.0	13.10 ± 1.3	5.6 ± 0.5	1667 ± 161

*mg/100 g fresh weight. **TRAP, total radical-trapping antioxidant potential.
Source: Goristein et al. (2001).

antioxidant capacity (TRAP) was significantly higher in peels than in the peeled fruits. The same results were obtained for the hydroxycinnamic acids (ferulic, sinapic, *p*-coumaric, and caffeic acids) found in the citrus fruits (Table 1.11).

Citrus peel also contains higher amount of flavonoids than the edible portion. Neoericitrin, naringin, and neohesperidin are the main flavanones in the peels of sour orange (*C. aurentium*), lemon (*C. limon*), and bergamote (*C. bergamia Fantastico*). Hesperidin is the main flavonoid in Valencia, Navel Temple, and Ambersweet orange peels, and naringin is the most abundant flavonoid in grapefruit. Also, diosmetin derivatives are the flavone compounds found in navel orange and lemon peels (Wang et al. 2008). Comparing the results found in eight different citrus fruits produced in Taiwan, Wang et al. (2007, 2008) found that both total flavonoid and total carotenoid contents were higher in the

Table 1.11 Total flavonoid and carotenoid content (mg/g dw) in peel and edible portion of different citrus fruits.

Citrus fruit Scientific name	Part of citrus fruit	Total flavonoids	Total carotenoids
C. reticulata Blanco	Peel	49.2 ± 1.33	2.04 ± 0.036
	Edible portion	11.2 ± 0.32	0.198 ± 0.0008
C. Sinensis (L.) Osbeck	Peel	35.5 ± 1.04	0.445 ± 0.008
	Edible portion	15.7 ± 0.43	0.080 ± 0.002
C.reticulate x C. sinensis	Peel	39.8 ± 1.02	1.59 ± 0.011
	Edible portion	11.1 ± 0.34	0.336 ± 0.005
C. Limon (L.) Bur	Peel	32.7 ± 1.06	0.110 ± 0.001
	Edible portion	21.6 ± 0.57	0.061 ± 0.001

dw, dry weight.
Source: Wang et al. (2007, 2008).

peels than in the edible part of the fruits (Table 1.11). Thus citrus peel is an important source of flavonoids that have a wide range of biological effects, such as antioxidative, anticancer, antiviral, and anti-inflammatory activities (Harborne and Williams 2000).

Citrus fruits have another health benefit: phytochemicals called limonoids, very high-oxygenated terpenoids. Limonoids appear in large amounts in citrus juices and citrus pulp as water-soluble glucoside derivatives, and in citrus seeds as water-insoluble limonoid aglicons. These are the compounds responsible of the bitterness in unripe fruits and are converted to nonbitter glucoside derivatives during fruit ripening. The main limonoids found in citrus fruit by-products are limonin, nomilin, and nomilinic. Limonoids have antiviral, antifungal, antibacterial, antineoplastic, and antimalarial activities. Some of them, such as azadirachtin, are also insecticides (Djilas et al. 2009).

1.5.2 Apples (*Malus domestica*)

Apple fruit (*Malus domestica*) belongs to the *Rosaceae* family and is harvested in the majority of countries in the world, with total production in 2011 of 75.48 million tons, China being the first producer with 50% of world apple production, with 35.98 million tons, followed by Europe with 15.19 million tons and the United States with 4.27 million tons. Apple pomace is the main by-product obtained by crushing and pressing during the clear juice recovery, and represents 25–35% of the fresh fruit weight. Apple pomace, consisting of peel, seeds, core, stems, and exhaustive soft tissue, has been widely studied for its antioxidant properties and beneficial effects on human health that have been demonstrated by numerous *in vitro* assays such as strong inhibitory activity of tumor-cell proliferation and human LDL cholesterol oxidation (Djilas et al. 2009; Grigoras et al. 2013; Thilakarathna et al. 2013). Several studies have identified the presence of important bioactive compounds such as polyphenols, minerals, dietary fiber, and also terpenoids. Apple pomace has been shown to be a good source of polyphenols, which are predominantly localized in the peels and are less extracted into the juice. Major phenols identified included derivatives of benzoic acids (gallic acid), hydroxycinnamic acids (chlorogenic acids), flavanols (catechin), flavonols (rutin and quercetin), and dihydrochalcones (phloridzin and phloretin-2′-xyloglucoside). Among the triterpenes, ursolic acid and oleanolic acid were the most abundant. These compounds also have many beneficial health properties such as anti-inflammatory, antimicrobial, antimycotic, antioxidant, antiviral, liver protective, immunomodulatory, hemolytic, or cytostatic effects (Muffler et al. 2011). The phenolic profile and antioxidant capacity of apple pomace is mainly related to the apple cultivars employed in fruit juice processing, the growing conditions of the apple tree, and the season (Diñeiro García et al. 2009; Grigoras et al. 2013).

1.5.3 Grapes (*Vitis vinifera*)

Grapes are a fruit that belongs to genus *Vitis* of the *Vitaceae* family. Grapes are an important world crop, with a production of 58.5 million tons in 2011, China being the first producer (9.17 million tons) followed by the United States (6.75 million tons) and Mediterranean countries such as Italy (7.11 million tons), France (6.58 million tons), and Spain (5.80 million tons). Commercially cultivated grapes can usually be classified as either table or wine grapes, based on their intended method of consumption: eaten raw (table grapes) or used to make wine (*Vitis vinifera*). Therefore, grapes can be eaten raw or used to produce wine, juice, jam, jelly, grapeseed oil, raisins, and vinegar. Approximately 71% of world grape production is used to produce wine, 27% as fresh fruit, and 2% as dried fruit. Grape pomace is a by-product of the wine industry and represents about the 20–25% of the weight of grapes crushed for wine production. The composition of grape pomace varies considerably depending on the grape variety and technology used to produce wine. Grape pomace is constituted by peels (skins), seeds, and stems, and is very rich in extractable phenolic compounds (10–11% of dry weight), mainly anthocyanins, catechins, procyanidins, flavonol glycosides, phenolic acids, and stilbenes (Yu and Ahmedna 2013). The seeds constitute a considerable portion of the grape pomace, amounting to 38–52% on a dry matter basis. Grape seeds are rich in phenolic antioxidants such as phenolic acids, flavonol glycosides, flavan-3-ols (catechin, epicatechin, and epicatechin-3-*O*-gallate), and stilbenes as resveratrol, while grape skins contain abundant anthocyanins. Grape seeds also contain 13–19% of oil rich in unsaturated fatty acids (mainly linoleic acid), about 11% of protein, and 60–70% of nondigestible carbohydrates, and other antioxidants such as tocopherols and beta-carotene (Djilas et al. 2009).

Flavan-3-ols are detected in the grape pomace derived from seeds and are catechin, epicatechin, epicatechin-3-*O*-gallate, gallocatechin, and their polymers.

Flavan-3-ols easily condenses into oligomeric procyanidins and polymeric compounds (condensed tannins). The dimeric procyanidins found in grape pomace are procyanidin B1, procyanidin B2, and procyanidin B4, and the trimeric procyanidins C1 and C2.

Polyphenol composition of grape pomace depends on the grape variety, the growing area, climate, maturity, and wine vinification method. Thus, red grape varieties are very rich in anthocyanins, mainly located in the skin (69–151 mg/kg fw); meanwhile, flavan-3-ols are the main phenolic compounds in white varieties (52–81 mg/kg fw) (Cantos et al. 2002). There are numerous published studies about the polyphenolic composition of grape pomace from different grape varieties in different wine-producing regions in the world (e.g., Yu and Ahmedna 2013). Thus, pomace from grape varieties widely produced in Brazil (Cabernet Sauvignon, Merlot, Bordeaux, and Isabel) showed that total phenol content ranged from 46.23 mg/g in Merlot to 74.75 mg/g in Cabernet Sauvignon, and total anthocyanins ranged from 7.02 mg/g in Cabernet Sauvignon and 11.22 mg/g in Bordeaux, being catechin the major nonanthocyanin compound identified (150 mg/kg). The anthocyanin content of grape pomace also varies with the variety and wine vinification method employed. Anthocyanins identified in grape pomace include 3-*O*-monoglucosides and acetylglucosides of delphinidin, cyanidin, petunidin, peonidin, and malvidin. Malvidin-3-*O*-glucoside was found to be the predominant anthocyanin.

Resveratrol is another important polyphenol found in grape pomace, which comes mainly from the skin. Resveratrol content varies with the grape variety and maturity. Muscadine grapes contain more resveratrol than other types of grapes. The average resveratrol content in white grape skin is 8.64 mg/100 g of dry mass and in white grape seeds is 1.42 mg/100 g of dry mass. Some studies have shown that resveratrol content in grapes could be increased by postharvest technologies such as cold storage or UV irradiation. It is important to note that although certain amounts of resveratrol transfer into wine, the majority remains in the grape pomace (Yu and Ahmedna 2013).

Finally, grape pomace contains a great content of nonextractable polyphenols, mainly consisting in high-molecular-weight proanthocyanins and polyphenols complexed with protein and cell wall polysaccharides. The nonextractable polyphenols was quantified in red grape pomace in 67 mg/g of dry mass and in white grape pomace in 1.68 mg/g of dry mass (Pérez-Jimenez et al. 2009).

Health benefits of consumption of grape pomace extracts are known for producers, researchers, the food industry, and the nutraceutical industry for many years. Numerous *in vitro* and *in vivo* studies have demonstrated that grape pomace phenolic compounds have many health benefits such as antimutagenic and anticarcinogenic activity, in addition to antioxidant and anti-inflammatory activities, prevention and delay of cardiovascular diseases, increase in lifespan, and delayed onset of age-related markers. In addition to antioxidant and beneficial health properties, there are numerous studies that show antibacterial activity of grape pomace extracts. Also, resveratrol, which is rich in grape skin, has antifungal and antibacterial activities. There are numerous reviews that summarize the most recent studies about the phytochemical composition of grape pomace and their biological properties and human health benefits (Yu and Ahmedna 2013).

1.5.4 Tropical fruits

Tropical fruit production, trade, and consumption have increased significantly due to their attractive sensory properties and a growing recognition of their nutritional and health-promoting properties (Ayala-Zavala et al. 2011; Correia et al. 2012). Examples of tropical crops include mango, papaya, pineapple, passion fruit, acerola, cashew apple, guava, longan, jackfruit, avocado, tamarind, sapodilla, and others. There is now a special interest from researchers, producers, health authorities, and the food, nutraceutical, and pharmaceutical industries in the study of pulps and by-products of tropical fruit to isolate specific phytochemicals for application in nutraceutical supplements, dietary additives, and new food and pharmaceutical products. These studies also contribute to the recovery of agro-industrial process waste, with major industrial, economic, and environmental impact (Ayala-Zavala et al. 2011).

Seeds, peels, and residual pulp are generated as solid by-products of the fruit processing industry. For instance, mango, papaya, and pineapple by-products represent from 35 to 60% of the fruit weight. The most bioactive compounds found in tropical fruit by-products are vitamins C and E, dietary fiber, and phenolic compounds. In general, vitamin C is uniformly distributed in fruits, carotenoids occur mainly in the external pericarp and peel, and phenolic compounds are located preferentially in peel and seeds. Table 1.12 shows the phenolic content in different parts of the fruit; it is noteworthy that the peel has higher phenolic concentration than the pulp. Also, Table 1.12 shows the total

Table 1.12 Total phenolic content (g/kg dw) of by-products from different mango cultivars.

Mango cultivar	By-product	Total phenolic (g/kg dw)
Tommy Atkins	Peel	25.13
	Seed	200.05
Kent	Peel	91.21
	Seed	191.25
Van Dyke	Peel	59.09
	Seed	70.10
Fafá	Peel	52.28
	Seed	149.33

Source: Barreto et al. (2008).

phenolic and carotenoid content of several tropical fruit by-products compared with their corresponding pulps. Therefore, tropical fruit by-products that are composed mostly of peels and seeds are a good source of phenolic compounds with biological activities beneficial for human health (Ayala-Zavala et al. 2011).

Taking into account the potential anti-inflammatory and antioxidant properties of tropical fruit by-products, numerous studies on the composition of bioactive compounds of these by-products have been reported and summarized in recent reviews (Ayala-Zavala et al. 2011; Correia et al. 2012; Silva et al. 2014).

1.6 Pretreatment and extraction systems

An important step in the production of phytochemicals from plant processing by-products is the stabilization and preparation of these for extraction (O'Shea et al. 2012). The difficulties found for the stabilization and preparation of by-products are:

- *Heterogeneous starting material* (cultivars, processing conditions, etc.), which makes it difficult to control yields and final prices.
- *Biological instability* of the by-products due to the high microbial load of these wastes, which can accelerate the degradation of phytochemicals and other nutritional compounds such as proteins, in addition to making the product unsafe.
- *High water content* (70–90%) of the plant by-products that makes transport to the recycling plant more difficult due to its high weight. Also pretreatments for the extraction of phytochemicals from by-products with high water content are more complicated. Due to the high water content of some by-products (71% in tomato, 90% in artichoke, and 82% in beet), the drying process (60 °C) and subsequent pressing involves high cost (Peschel et al. 2006). Furthermore, pressing presents an additional problem since the water obtained has a high content of organic substances and has to be recycled.
- *Oxidation of by-products with a high fat content* (avocado) can lead to the development of unpleasant odors from the oxidation of fatty acids.
- *Enzymatic activity of plant residues*. The enzymes remain active and may accelerate the degradation process, which leads to the loss of valuable phytochemicals or bioactive compounds. The thermal treatment or blanching (85–100 °C) prior to the extraction of phytochemicals from by-products may be useful to inactivate the enzymes that cause various degradative processes such as enzymatic browning. As an alternative to traditional blanching, ohmic heating can be employed, which is a homogeneous and faster electrical heating that reduces the loss of heat-sensitive phytochemicals such as vitamin C (Icier 2010).
- *Pretreatments*. For extracting phytochemicals from vegetable by-products, various pretreatments are required: wet grinding of the by-product (for reducing the particle size of wet residue) and drying (oven, lyophilization) and grinding the dried extract to achieve the required particle size (O'Shea et al. 2012.). The

stabilization of the by-products before being subjected to extraction is a critical phase that requires the study of the most suitable conditions to prevent degradation of phytochemicals or bioactive compounds. For example, in the case of onions, mild heat treatment (pasteurization) and the freezing/freeze-drying of their by-products have been the best pretreatments to preserve the stability of their phytochemicals (Roldán et al. 2008; Benítez et al. 2011).

- *Extraction*. The traditional method of solid–liquid extraction using a Soxhlet with organic solvents is a process that requires time and large amounts of solvents (Ayala-Zavala et al. 2011). Enzymatic treatments with enzymes such as pectinase and cellulose, capable of degrading the cell wall constituents and to facilitate the extraction of phytochemicals such as lycopene from tomato skins, have been also employed in the industry (Choudhari and Anantharayan 2007). An interesting alternative to conventional solvent extraction is supercritical fluid extraction, primarily with supercritical carbon dioxide (SC-CO_2), and also the extraction with solvent under pressure generally known as extraction with subcritical water (Wijngaard et al. 2012). These technologies have the disadvantage of being expensive but may be of interest in terms of economic value and functional characteristics of phytochemical compounds extracted. This is the case of lycopene, a valuable functional ingredient of high economic value, that lost its biological activity as a consequence of degradation and isomerization caused by heat treatment (Lennuci et al. 2010). Also being studied is the use of new extraction technologies such as low-intensity electrical pulses, ultrasonic, and microwave (Wijngaard et al. 2012).

Finally, it should be kept in mind that before using functional ingredients obtained from plant processing by-products, additional studies are needed, such as toxicological studies, to ensure that the ingredient is free of pesticides and other undesired or toxic substances. Bioactivity studies are also required to enable us to determine the bioaccessibility and bioavailability of phytochemicals extracted from these by-products. Regulation (EC) 1924/2006 on nutrition claims on foods requires that any declaration (within the permitted) has to be based on scientific evidence. Therefore, the correct characterization of plant by-products and their corresponding extracts is critical for potential commercialization.

Therefore, the industrial production of phytochemicals derived from by-product processing plants and their use as functional ingredients in foods requires the coordination of interdisciplinary studies from food technologists, food chemists, nutritionists and toxicologists.

In conclusion, agro-industrial by-products are a good source for obtaining phytochemicals with high antioxidant activity and other beneficial health properties. In addition, the exploitation of these abundant and low-cost renewable resources could be anticipated for the pharmaceutical, nutraceutical, and food industries with the opportunity of developing new nutraceutical and/or pharmaceutical products. Also, this form of recuperation of by-products is an interesting way to reduce industrial waste, cost, and environmental impact generated by the habitual destruction of by-products, with the added value of obtaining phytochemicals with beneficial health properties. From the point of view of the consumer, the general use of natural additives to replace synthetics is a healthy advantage. In general, additives from vegetable processing by-products are perceived by consumers as a more natural ingredient; besides, its consumption can provide beneficial health effects.

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