Chapter 20

Onions: A Source of Flavonoids

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Abstract

Flavonoids are a large and diverse group of polyphenolic compounds with antioxidant effects, and onion (*Allium cepa* L.) is one of the richest sources of dietary flavonoids. Flavonoid content is affected by endogenous factors—genotype and agro-environmental conditions. Considerable research has been directed toward understanding the nature of polyphenols in different products and the factors influencing their accumulation. This review examines the impacts of pre- and postharvest factors on onions' flavonoid content, highlighting how this knowledge may be used to modulate their composition and the potential use of onion by-products.

Keywords: polyphenols, plant foods, *Allium cepa*, preharvest factors, harvest handling, genotype

1. Introduction

Phenolic compounds are responsible for the major organoleptic characteristics of plant-derived foods and beverages, particularly color and taste properties, and they also contribute to the nutritional qualities of fruits and vegetables [1, 2].

Plants present diverse defense mechanisms, including physical and chemical barriers. Phenolic compounds are particularly abundant and play an important role in both strategies, as monomers for the synthesis of lignin and as chemical agents. Flavonoids are one of the most relevant secondary compounds in plants and currently more than 9000 being identified [3]. A most significant function of the flavonoids, especially the anthocyanins, together with flavones and flavonols as copigments, is their contribution to flower and fruit colors. This is important for attracting pollinators and seed-dispersing animals. Phenolics may influence the competition among plants “allelopathy.” They act in plant defense mechanisms against herbivores or pathogens, contributing to the disease resistance mechanisms in plants, and act as supporting materials of cell walls as photoprotectors against UV radiation and plant-microbe symbiosis and involved in the repair of wounds and contribute to healing by lignifications of damaged areas. Stress conditions such as excessive UV light, wounding, or infection induce the biosynthesis of phenolic compounds [66, 67].

Plants composition can be affected by pre-harvest factors, including genotype (cultivar and variety), maturity at harvest and tissue distribution, and exogenous factors, including climate, soil micro-environment, and pest and disease attack [4, 5]. Environmental factors have a major effect on polyphenol content. These factors may be pedoclimatic (soil type, sun exposure, and rainfall) or agronomic (culture in greenhouses or fields, biological culture, hydroponic culture, fruit yield per tree, etc.). With the current state of knowledge, it is difficult to determine for each family of plant products the key variables that are responsible for the polyphenol variability. A huge amount of analysis would be required to obtain this information [10].

This paper reviews recent literature on the main factors affecting the flavonoid content in onion, as well as different approaches aiming to increase the accumulation of these compounds in onions, which provide an added functional value.

2. Occurrence and identity of flavonoids in onions

Onion has been reported as one of the major sources of dietary flavonoids in many countries [6–9], contributing to a large extent to the overall intake of flavonoids [10, 11]. Two flavonoid classes are mainly found in onion, the anthocyanins, which impart a red/purple color to some varieties, and flavonols such as quercetin and its derivatives, responsible for the yellow and brown skins of many other varieties (see **Table 1**).

Flavonols are the most ubiquitous flavonoids in onions. At least 25 different flavonols have been characterized in onion, being quercetin derivatives the most important ones in all onion cultivars [11]. Quercetin 4′-glucoside and quercetin 3,4′-diglucoside are reported as the main flavonols in onions, accounting for about 80–95% of total flavonols [12–26].

The quantitative content of anthocyanins in some red onion cultivars has been reported to be approximately 10% of the total flavonoid content or 39–240 mg kg^{-1} FW [11]. In red onions more than 50% of anthocyanins are cyanidin glucosides non-acylated or acylated with malonic acid. Delphinidin and petunidin do not have malonyl derivatives in detectable amounts, indicating that the presence of malonylated derivatives seems to occur only in the cyanidin derivatives [27]. Some of these pigments facilitate unique structural features like 4′-glycosylation and unusual substitution patterns of sugar moieties. Altogether at least 25 different anthocyanins have been reported from red onions, including 2 novel 5-carboxypyranocyanidin-derivatives [28].

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Class	Flavonoid	mg/100 g FW	Reference
Total polyphenols			
		438.88 (Y) (DW)	[132]
		35.00	[133]
		443.20	[135]
		253.60–310.80 (R)	[136]
		216.70 (W)	[136]
		129.60	[137]
		73.33–180.84	[138]
		66.80	[139]
		76.10	[140]
		116.00 (R)	[141]
		70.00 (W)	[141]
		24.40 (W)	[142]
		154.10	[143]
		260.00–650.00 (W) (DW)	[144]
		21.60–58.30	[145]
Total flavonoids		12.21–52.43	[138]
		0.18 (W)	[15]
		69.20 (Y)	[29]
		76.58 (Y)	[15]
		61.05 (R)	[15]
		18.70	[143]
		56.00–1150 (W) (DW)	[144]
		35.3 (R)	[146]
Total flavonols		7.90–43.10 (R)	[148]
		9.85 (Y) (μmol/g DW)	[149]
		8.90–177.80	[22]
		55.40–62.10 (R)	[150]
		35.00–159.2	[50]
		28.55–51.64 (Y)	[14]
		58.09 (R)	[14]
	Quercetin aglicone	0.07 (W)	[15]
		111.70 (Y)	[22]
		5.00 (W)	[22]

Class	Flavonoid	mg/100 g FW	Reference
		105.2 (P)	[22]
		137.50 (R)	[22]
		0.50–9.90	[50]
	Total quercetin		
		8.11 (Y)	[15]
		23.95 (R)	[15]
		7.70–46.32	[138]
		28.40–48.60	[151]
		54.40	[152]
		6.17 (W)	[153]
		39.21 (R)	[153]
		19.20 (Y)	[154]
		30.70 (R)	[154]
		30.60 (R)	[155]
	Q. total (after hydrolysis)	22.00–48.00 (Y)	[156]
	″	237.03 (Y) (DW)	[132]
		83.00–330.00 (Y) μg/g	[26]
	Q. 3′-glucoside	1.70–2.30 (R)	[150]
		0.30	[16]
		0.76	[157]
		0.30–2.60	[50]
	Q. 4′-glucoside	20.80–23.00 (R)	[150]
		3.60 (W)	[22]
		36.00 (Y)	[22]
		30.20 (P)	[22]
		39.40 (R)	[22]
		9.70	[16]
		0.11 (W)	[15]
		57.18 (Y)	[15]
		13.77–26.75 (Y)	[14]
		30.01 (R)	[14]
		30.01 (R)	[27]
		29.89 (R)	[15]
		19.00–95.20	[50]
		33.08 (Y) (DW)	[132]

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Class	Flavonoid	mg/100 g FW	Reference
	Q. 3,4′-diglucoside	25.40–27.40 (R)	[150]
		20.22 (R)	[158]
		11.37–21.11 (Y)	[14]
		20.22 (R)	[14]
		4.92 (Y)	[15]
		2.48 (R)	[15]
		40.50	[16]
		111.70 (Y)	[22]
		5.00 (W)	[22]
		105.20 (P)	[22]
		137.50 (R)	[22]
		11.60–45.50	[50]
		241.04 (Y) (DW)	[132]
	Q. 7,4′-diglucoside	0.70–1.10 (R)	[150]
	Q. 3,7,4′-triglucoside	0.60–0.90 (R)	[150]
	Kaempferol	1.54–1.83	[138]
	Myricetin	2.77–4.13	[138]
	Isorhamnetin	5.19 (Y)	[15]
		0.63–5.04 (R)	[15]
	I. 4′-glucoside	4.10–4.90 (R)	[150]
		3.40 (R)	[15]
		1.20–710	[50]
		6.00 (R)	[159]
	I. 3,4′-diglucoside	2.10–2.50	[150]
		0.30–1.50	[50]
Anthocyanins	Total	7.00–21.00 (R)	[160]
	Cyanidin	3.19 (R)	[153]
	Cyanidin 3-O-(6″-malonyl-glucoside)	1.50 (R)	[27]
	Cyanidin 3-(6″-malonyl-3″-glucosyl-glucoside)	1.00 (R)	[27]
	Delphinidin 3-glucosyl-glucoside	6.50 (R)	[27]

DW, dry weight; FW, fresh weight.

Table 1. Phenolic compounds in onion (onion color: P, pink; R, red; Y, yellow; and W, white).

Flavonoids comprise a generous portion of the total antioxidant activity in onions [29]. Elhassaneen and Sanad [30], in a study with Egyptian onion varieties, concluded that phenolic compounds, particularly the flavonol quercetin, beside other factors including selenium and sulfur-containing amino acids, play the major role in the antioxidant activity of onion bulbs.

2.1. Approaches for the accumulation of antioxidant flavonoids in onions

Flavonoids play a lot of roles in plant physiology, mainly related to plant resistance [31, 32], in defense mechanisms against herbivore and pathogen attacks, UV radiation protection, plant-microbe symbiosis. They contribute, as copigments, to flower and fruit colors, especially the anthocyanins, flavones, and flavonols [33], important plant characteristic for attracting pollinators or seed-dispersing animals and allelopathy [34]. Flavonoids have also been shown to modulate transport of the phytohormone auxin [35] as well as the levels of reactive oxygen species (ROS) [36].

Thus, the strategies applied to obtain plant foods with higher level of flavonoids, increasing their functional value, must be based on the manipulation of interacting factors (genetic, environmental conditions, and agronomic practices) that are known to affect their content [4, 129].

The great challenge, due to the vast variables involved (intraspecific chemodiversity, genetic and ontogeny, postharvest, and biotic and abiotic factors) [129], is the implementation of a large-scale and low-cost suitable production systems to obtain onions rich in flavonoids with the maintenance of balance between phytochemical content and agro-production. An interdisciplinary overview and data collection, analysis, and evaluation of scattered data regarding the diverse factors involved in the optimization of plant production and postharvest and processing management are fundamental [37].

The plant needs to recognize the agro-environmental stimuli (see exogenous factors in **Table 3**), which is dependent on the sensitivity of organs and tissues and influences the metabolic response, depending on the gene expression transcribed to functional enzymes. Then, metabolic channeling may induce the accumulation of the target product. The agronomic activities, including climate modeling, modifying secondary metabolism, and the correspondent bioactive compound produced, may change plant physiological activity and affect their development and productivity [38].

2.1.1. Approaches based on endogenous factors

Research on genetics and plant metabolism has started, in the last years, to become interested in crop development with enhanced phytochemical concentrations. Although the genetic impact seems to be greater than the external factors, the synergistic effect of genetics with specific agronomic approaches could have a stronger capacity on improving certain phytochemicals. However, it is extremely complex to implement preharvest strategies to maximize the biosynthesis of specific phytochemicals and simultaneously maintain the level of productivity and other qualitative parameters of the products. Progress toward understanding the impact of key strategies will allow their integration into sustainable agricultural production systems aimed to alter the content and/or profile of phytochemicals in new crop varieties [39]. The main endogenous factors that affect onion flavonoids are summarized in **Table 2**.

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2.1.1.1. Cultivar selection

Onion flavonoid content is highly explained by genetic factors [15], probably due to the diversity of onion cultivars, hybrids, and open pollinated. The genetic makeup of the onion varieties needs to be factored in when differences in flavonoids content and antioxidant activity are considered [29, 134].

Lee and Mitchell [40] studied six commercial onion varieties in which quercetin content ranged up to 18-fold between 93 and 1703 mg/100 g DW. The highest level has detected in a yellow, early, and long-day variety "milestone."

The flavonoid profile affects the color of onion bulbs. Red cultivars generally contain higher total flavonoid content [11, 20, 30, 41–43], because they are richer in flavonols but also contain anthocyanins, unlike white varieties. Dalamu et al. [44] evaluated 34 onion genotypes and verified great variation in total phenolic content between white (165.0), pink (702.0 mg kg^{-1}), and red varieties (867.8 mg kg^{-1}) which means an overall more than fivefold variation. Red onions, with highest levels of phenolics, also have about three times higher antioxidant activity than white onions. The quercetin content in these 34 genotypes ranges from 22.0 to 890.5 mg kg^{-1}. The largest variation occurred in yellow cultivars [11]. Patil et al. [45], in a study with 55 cultivars of yellow onions, verified a variation from 54 to 286 mg kg^{-1} FW in quercetin content. Grzelak et al. [12] also reported differences between three yellow onion varieties in flavonol glucosides and total flavonol content but no statistical differences between harvest seasons.

Quantitative data compilation presented in **Tables 1–3** indicates a great diversity in flavonoid content among the cultivars surveyed. Total phenolic content in onion genotype seems to present a definite hierarchy, highest in red and lowest in white. In contrast, Crozier et al. [46] reported the opposite but only for quercetin; they found only 201 mg kg^{-1} of quercetin in edible parts of red onion but much higher quercetin amount in white onions (185–634 mg kg^{-1}). Marotti and Piccaglia [15] also found higher levels of total flavonoids in a golden variety "Dorata Density," in relation to other different color varieties (including red onion).

There are many reports in the scientific literature on how resistant cultivars of different crops contained more phenolic compounds than susceptible ones suggesting that these compounds play an important role in the defense mechanism [47, 48]. Lachman et al. [49] found different profiles in polyphenol content between susceptible and resistant onion cultivars. Yang et al. [29] concluded that onion varieties, which have strong, bitter, and pungent flavors and high sugar contents, exhibited higher antioxidant and antiproliferative activities. Vågen and Slimestad [50], in 15 cultivars studied, also detected a positive correlation between pungency, amounts of fructooligosaccharides (FOS) and flavonols, and the highest Trolox equivalent antioxidant capacity (TEAC) values.

Okamoto et al. [51] reported differences in quercetin content between short-day and long-day onion cultivars. The long-day cultivars from Northern Europe and their close relatives contain higher concentrations of quercetin glucosides than those of Japanese and North American. In long-day cultivars, total quercetin content was higher than in short-day cultivars being independent of the growing origin [51, 52].

Factor	Evaluated parameters	Effect on flavonoids	References
Varietal differences	Different bulb colors	Red > yellow > gold *Exception	[46]* [49] [42] [15]* [11] [43] [41] [30] [44] [20]
	Yellow varieties		[45] [11] [12]
	Resistant and susceptible onion cultivars	Resistant > susceptible	[49]
	Long-day and short-day onion cultivars	Long-day > short-day	[51] [52]
Size and bulb weight		No differences *Small > large	[45] [64] [61]* [20]*
Bulb parts	Scales	Dry outer skins > outer edible > middle edible > inner edible *Exception: middle layers > outer scales > inner layers	[63] [55] [57] [27] [64, 65] [61] [56] [12] [60] [62]*
	Top to bottom	Top > bottom	[63] [57] [20]

Table 2. Endogenous factors affecting the accumulation of flavonoid in onions.

2.1.1.2. Tissue selection

Although flavonoids are derived from the same biosynthetic pathway, they accumulate differentially in plant tissues, depending on the developmental stage and the environmental conditions, since they fulfill different physiological functions [53]. The plant prioritization defense strategy to allocate defense compounds to the most valuable tissues can explain why young leaves have more phenolics than mature leaves. Tissues such as skin scales, with protective function, appear to have the same strategy. Similarly, ontogenetic changes in defensive allocation in seedling and juvenile plants may also be an evolutionary response to herbivore at this particularly susceptible stage of a plant's life cycle [54].

Factor	Evaluated parameters	Effect on flavonoids	References
Soil type		Clay > sandy loam	[70]
Fertilization	N levels	No differences in quercetin	[80]
	NH_4^+:NO_3^- ratios	>Dominant nitrate supply	[72]
	Varieties Kamal and Robin (N and S)	Positive correlation with N and S fertilization	[146]
	White variety of Pueblo and yellow variety of Mundo were the most efficient when fertilized by nitrogen and sulfur in combination with iron	Positive correlation with N, S, and Fe fertilization	[147]
Mycorrhizal colonization/ inoculation		>Quercetin	[72]
		No effects	[64]
Organic versus conventional		Organic > conventional	[78] [81]
	Organic fertilizers, and no chemical herbicides or fungicides, or inorganic fertilizers	No differences	[64] [80]
Chemical treatments	Benzothiadiazole and K_2HPO_4 to control *Stemphylium*	>Phenolic	[85]
Yearly variation			[64] [80] [25]
Light	Global radiation in the end of production period	>Radiation > flavonoids	[64]
	Total global radiation during production period	>Radiation > flavonoids	[25]
	UV light lamps after harvest	>Quercetin	[77]
	Fluorescent light after harvest	>Flavonoid	[61]
CO_2	Elevated to 550 ppm in relation to atmospheric (365 ppm)	<Flavonoid >Anthocyanins and total phenols	[162]
Lifting	Lifting time	Late lifting > early lifting	[71]
Curing			[123]
	Evolution in relation of levels at harvest	After curing > at lifting	[70] [64] [23]
		Field > dark environment *Field curing: dark similar to light exposed	[64] [23]

Table 3. Exogenous factors affecting the accumulation of flavonoid in onions.

The outer onion skin-dry peel scales have more total flavonoids than the edible flesh scales [27, 55, 56]. Hirota et al. [57] found that outer scales and the upper portions of the edible scales had higher levels of 4′-Qmg and 3,4′-Qdg and Qag than lower (internal) scales.

The flavonol glucoside hydrolysis during the peel formation can explain why aglycones are the main flavonoids present in the peel [22, 58]. Quercetin is concentrated in the dry skin of most onions where its oxidation products, 3,4-dihydroxybenzoic acid, and 2,4,6-trihydroxyphenylglycosilic acid impart the brown color and provide the onion bulb protection from the soil microbial infection [58, 59]. Bilyk et al. [55] observed that as much as 53% of the total quercetin in onion skin was present as aglycon, occurring great differences between dry skin and edible scales. The dry skin of onion bulbs of red and pink varieties is richer in flavonols and anthocyanins, mainly in aglycon forms. In red onion, the dry skins contain ~63% of total anthocyanins present in bulb. It means that only 27% of the total anthocyanins will be consumed after bulb peeling [27].

Slimestad and Vågen [60], in edible scales, detected higher quantities of flavonols and fructose and simultaneously the highest antioxidant capacity in the outer fresh scales. An abrupt drop in flavonol quantity occurred from the first to the second scale, followed by a slight decrease further inward. Grzelak et al. [12] also reported that outer edible fresh scales of the bulb have threefold of mono- and diglucosides of quercetin and isorhamnetin than inner scales. Outer scales of triglycosides have ca. 1.5-fold greater in the middle scales. A graduated decrease in flavonoids, from the first to the seventh scale, was also observed in onion bulb [61]. Inversely to other authors, Beesk et al. [62] verified the following distribution order in scales of the flavonoid content: middle layers > outer scales > inner layers. Qdg was the major flavonoid in the inner layers, Qdg and Qmg were in equal amounts in the middle layers, and quercetin was the major flavonoid in outer scales followed by Qmg. Trammell and Peterson [63], considering vertical distribution, found that the flavonoid is presented in higher amounts (by twofold) in top than bottom (disk) of the bulbs. A two- to threefold increase in concentration from the center of the bulb outward is observed in a horizontal bulb distribution. The least pigmented line showed a 17-fold increase and had 56% of its total flavonols in the outer scale compared with about 30% for the other lines. Mogren et al. [64, 65] and Lee et al. [61] reported comparable gradient in total quercetin composition in the edible onion scales indicating that 90% of total flavonols are in epidermal tissue. Parenchymous storage tissue, the bulk of a bulb, only contains around 10% of the total pigment. It follows that any factors which modify the ratio of epidermal to storage tissue scale, including thickness, could indirectly change gross flavonol concentration.

In onion, quercetin concentration does not appear to be affected by bulb size or weight, and small bulbs contain the proportional quercetin concentration as larger bulbs [45]. Mogren et al. [64] obtained results that showed minor or no differences in quercetin glucoside content among small-, medium-, or large-sized onions, although Lee et al. [61] and Pérez-Gregorio et al. [20] detected higher flavonoid content in small onions than in large ones.

2.1.2. Approaches based on exogenous factors

In addition to genetics, other factors can affect the onion bulbs' flavonoid contents, mainly related with pedoclimatic conditions, agronomic practices, and postharvest handling and

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processing. Being secondary metabolism an integral part of the plant capacity to adaptation to the surrounding environment, it is not surprising that these factors can modulate its phytochemical profile.

As polyphenolic compounds are part of a complex defense mechanism of plants, environmental stress factors such as pests and diseases, ozone and UV light, cold, and nutritional stress can induce their biosynthesis [66, 67]. Therefore, regulating environmental stresses provides an opportunity to enhance the flavonoid content of plants. Nevertheless, because of their potential adverse effects on crop growth, yield, and even in commercial quality (sensorial attributes), such approach should be considered with caution.

Treutter [38] made a compilation of agricultural technologies influencing the biosynthesis and accumulation of phenolic compounds in plants, including remarks on the effects of temperature light, mineral and organic nutrition, water availability and moisture stress, grafting, atmospheric CO_2, growth and differentiation of the plant and application of stimulating agents, elicitors, and plant activators.

Table 3 compiles studies about the main exogenous factors affecting the flavonoid content in onions, as well as different strategies targeting to increase their content.

2.1.2.1. Soil nutrient status

Accumulation of phenolic compounds in plant can be influenced by mineral, being a limited nitrogen supply generally linked with higher levels of phenolics [10]. This reaction can be explained by the activity increase of phenylalanine ammonia lyase (PAL) enzyme to obtain ammonia from phenylalanine, as a source of nitrogen for amino acid metabolism. Cinnamic acid, as a result of the deamination process, is also released and further incorporated into the phenylpropanoid synthetic pathway, increasing the phenolic synthesis [68]. On the other hand, nitrogen limitation will affect photosynthesis, decreasing chlorophyll availability and disrupting photosynthetic membranes due to starch accumulation, which can explain the increased sensitivity to light intensity. Synthesis of photoprotective pigments such as anthocyanins and flavonols may give protection against light-induced oxidative damage [69].

Patil et al. [70] observed higher amounts of quercetin in onions growing under nitrogen limitation in both clay and sandy loam soils. Despite this, the location of growth, more than soil type or growth stage, is a key environmental factor for quercetin levels in onion.

Mogren et al. [64, 65, 71] compared diverse applications of organic fertilizers, and it was found that the nitrogen fertilization did not affect the yield or quercetin glucoside content in the onion. Additionally, it did not find significant differences between onions with or without nitrogen fertilization in quercetin glucoside content. High levels of nitrogen (80 kg ha^{-1}) do not improve yield or quercetin glucoside levels in the onions. Thus, it is preferable to fractionally apply small amounts of nitrogen fertilizers because it reduces the risk of leaching of mineral nutrients without reducing the crop yield or quercetin content of onion bulbs.

Perner et al. [72] studied the effect of mycorrhizal colonization and different ammonium/nitrate ratios as nitrogen fertilizer on onion yield and nutritional characteristics. It was concluded that the organosulfur compounds, quercetin glycosides, and antioxidant activity can be increased in suitably supplied onion plants if nitrate is dominant. Quercetin glycosides and antioxidant activity are also increased with mycorrhizal colonization. This was possibly due to amplified precursor production and induced defense mechanisms.

As these compounds are produced as part of plant defense mechanisms against stress factors, water availability and regulated deficit irrigation might also modulate metabolic pathway and considerably affect plant phenolic composition [4]. Mohamed and Aly [163] observed that seawater salt stress causes a reduction in the total phenolic compounds.

2.1.2.2. Light

The intensity, quality, and photoperiod of light (sunlight spectrum and proportion of ultraviolet and the red/far-red ratio) are the main environmental factors affecting the flavonoid synthesis. The regulation of expression of several genes that encode the activity of enzymes participating in the phenylpropanoid pathway such as cinnamate 4-hydroxylase (C4H) or PAL, is affected by light conditions during plant development and storage, playing an important role in the phenolic compounds [1].

Flavonoids protect against UV radiation and accumulate mainly in the epidermal cells of plant tissues [73]. However, the response to UV radiation, of various plant species, can vary substantially in terms of flavonoid synthesis [67]. The synthesis of specific flavonoids and other phenolics can be differently regulated in response to UV light depending of plant species, and the contribution to UV stress protection can vary between phenolics [74]. Light stimulates flavonoid synthesis, particularly anthocyanins and flavones, being PAL the major inducible enzyme [66, 75].

The levels of quercetin glucosides in the external dry skins, exposed to light, are less than 10% of the levels in fleshy and partly dried scales. The probable mechanism is that quercetin is formed by deglucosidation of quercetin glucosides on the border between drying and dried brown areas on individual scales [57, 76].

In the end of onion bulb growth, the global radiation seems to be one of the major determinants on quercetin glucoside content [17–20, 23, 25]. Mogren et al. [64] observed that the lower the global radiation in the last month of bulb growth, the lower the content of quercetin. Postharvest treatment of onion bulbs with UV light or fluorescent light lamps can induce quercetin production [77]. Exposure of onion bulbs to fluorescent light for 24 and 48 h induced time-dependent increases in the flavonoid content [61].

2.1.2.3. Organic versus conventional production

Manach et al. [10] verified that vegetables produced by organic or sustainable agriculture contain higher polyphenol content than vegetables grown in conventional production or hydroponic systems. Two main hypotheses have been proposed to explain the potential increases in polyphenol compounds in organic versus conventional production of vegetables. One hypothesis considers the influences of nutrient management and fertilizer application on plant metabolism. Synthetic fertilizers, used in conventional agriculture, normally present higher availability nitrogen that may accelerate plant growth more than organic fertilizers. Consequently, plant resources are allocated mainly for growth, and the plant tends to invest less in the production of secondary metabolites such as amino and organic acids and polyphenols. The second hypothesis considers the plant reactions to biotic stress such as pests and diseases and weed competition. Organic production methods, which limit the use of agrochemicals such as insecticides, herbicides, and fungicides, may induce greater stresses on plants that tend to allocate more resources toward the synthesis of their own chemical defense compounds [161].

Ren et al. [78] detected 1.3–10.4 times higher levels of flavonoids, quercitrin, caffeic acid, and baicalein and in various organic vegetables onion than conventional, suggesting the influence of cultivation techniques. All green vegetables tested also had greater antioxidant activity in organic production.

Grinder-Pedersen et al. [79] verified differences in quercetin levels between organic and conventional onions, but because different cultivars in the two different production systems were studied, it cannot be ruled out that the differences were due to cultivar (genetic factor).

Mogren et al. [80] did not find significant differences on quercetin glucoside levels between onions organically produced and onion treated with chemical fertilizers. The conclusion could be that the nitrogen source, organic or inorganic, and the absence of chemical fungicides seemed to have no effect on quercetin biosynthesis.

Faller and Fialho [81] suggest that the effect of organic practices results in different effect patterns according to the plant species analyzed, with fruits being more susceptible to the induction of polyphenol synthesis than vegetables. Organic onion pulp had higher antioxidant capacity than conventional [81].

Søltoft et al. [82] also did not find significant differences in the flavonoid level between organic and conventional onions.

In Lee et al. [83] study the organic onions usually start bulbing later than conventional onions because of black plastic film and delayed nitrogen mineralization. That might be an important cause of the lower level of phenolics in organic onions.

2.1.2.4. Chemical treatments

Herbicide and, to a lesser extent, insecticide and fungicide application can also affect the synthesis of phenolic compounds in plants. Diphenyl ethers (e.g., acifluorfen) act as herbicide mainly by oxidative damages (singlet oxygen of protoporphyrin). Plants, when treated with herbicides, as a possible defensive reaction to the oxidative damages, increase the PAL synthesis and produce more flavonoids. The risks of the combined natural and pesticide-induced modulating effects on human health and environmental protection should be evaluated [84]. Kamal et al. [85] observed that onion plants treated with di-potassium phosphate and benzothiadiazole (Bion) presented significantly higher PAL and PO activity and phenolic contents than the untreated plants. It was concluded that application of chemical solutions such as di-potassium phosphate and benzothiadiazole applied for pathogenic control can enhance phenolic compounds in onion plants [85]. But, the risks of the combined natural and pesticide-induced modulating effects on human health and environmental protection should be further evaluated [84].

2.1.2.5. Harvest time and postharvest treatments

Many phytochemicals are synthesized in parallel with the overall development and maturation of fruits and vegetables. Therefore, their content in plants can considerably vary with different stages of maturity [10].

Total flavonol content increased as spring onion plants matured (226–538 mg/100 g at 14 and 77 days, respectively) [86]. In bulbs, harvest date has been reported to have almost no effect to onion bulbs [70].

Mogren et al. [71] found that late lifting of onions (80% fallen leaves) leads up to 45% higher concentrations of quercetin glucosides compared with early lifting (50% fallen leaves).

Onions left in the field, to curing, after harvest accumulates more flavonols [70]. Mogren et al. [64] also detected a dramatic increase in quercetin glucoside content during field curing (between 100 and 300%, during the 10–14 days of curing). Price et al. [21] demonstrated a 50% loss in quercetin monoglucoside during the initial curing process. Flavonol and anthocyanin levels in onions cured in the dark were similar to those obtained in bulbs cured in the light [23]. Mogren et al. [64] observed that field curing onions presented an increase in quercetin content significantly higher compared to the onions stored in dark conditions. Removal of the foliage to the bulb, before the process of field curing, did not affect quercetin content, suggesting that no transport occurs, in mature bulbs, between the foliage and scales. During field curing an increase in quercetin content occurred, particularly when the flavonol concentrations were low at lifting [23].

Rodrigues et al. [24] observed that total flavonols increased during storage of onion bulbs, but when stored under traditional storage (without controlled temperature) showed higher increases of flavonoid levels than those stored under refrigeration. Bulbs stored in the field (at fluctuating ambient temperature) reached higher levels of flavonoids (64% maximum) than refrigerated onions (40% maximum). Regarding anthocyanins, after 7 months in both conditions (refrigeration and traditional treatment), the whole anthocyanin content was reduced to more than 40%. Gennaro et al. [27] also observed a decrease to 64–73% of total anthocyanins in onions stored under domestic conditions, which seems to indicate that flavonol glucosides are more resistant than anthocyanins during storage. Ethylene accumulated during onion storage can stimulate activity of phenylalanine ammonia lyase (PAL), a key enzyme in biosynthesis of phenolic compounds and accumulation of phenolic constituents [87, 88], and justify the significant increase in flavonols observed during storage [24]. Benkeblia [87] reported a positive relationship between PAL activity and total phenolic variations in long-term stored onion bulbs.

The effect of onion bulbs' storage conditions in the composition of flavonoids was studied by several authors. Price et al. [21], apart from a 50% loss of quercetin 4-monoglucoside during the initial drying process (after curing at 28°C), observed little change in composition over 6 months of bulbs storage. Benkeblia [87] evaluated total phenolics in onion bulb during storage at 4 and 20°C and observed a variation in phenolics relatively regular at both temperatures. Lachman et al. [42] observed an increase of total flavonoids, especially at higher temperatures, at the end of 36 weeks of storage, in red and yellow onion varieties. Gennaro et al. [27] concluded that home storage habits resulted in a decrease to 64–73% of total anthocyanins, but degradation is slower when onions are refrigerated. Rodrigues et al. [24] also observed that after 7 months of storage, total anthocyanin content was reduced between 40 and 60%.

2.1.3. Processing

Onion flavonoid effects of domestic treatments like slicing [89–91], cooking [23, 92], or frozen [19, 93] were also studied. Onion products could be processed before consuming, but processing may result in losses in those valuable flavonoids. As was already referred, some researches focused on the effect of domestic processing techniques such as chopping, shredding, peeling, roasting, cooking, or boiling on flavonoid content, and depending on the severity of heat treatment, losses were evident. Furthermore, onion could be also industrially processed. Thus, industrial processing not only includes all domestic treatments referred but also includes the effect of sanitizing technologies as well as freezing, freeze-drying, dehydration, packaging, and stored processes. Through this section how these applications and storage affect the flavonoid content and profile will be described.

2.1.3.1. Fresh-cut technology

Fresh-cut fruit and vegetable products hardly increase their presence in the marketplace due to demand by the consumer. In the coming years, it is commonly perceived that the fresh-cut food industry will have unprecedented growth. However, processors of fresh-cut fruit products face numerous challenges not commonly encountered during fresh-cut vegetable processing. The difficulties encountered with fresh-cut fruit, while not insurmountable, require a new and higher level of technical and operational sophistication. Physical changes resulting of minimally processed food production could induce physiological and therefore compositional changes that could affect the final food quality. The effect on flavonoid content of minimally processed onion will be discussed in each step of food processing.

2.1.3.1.1. Cutting

Wounding stress was largely studied as increasing the phenolic content and antioxidant activity of vegetables [94–96]. According with Cantos et al. [90], the three most important enzymes related to phenolic metabolism, polyphenol oxidase, peroxidase, and phenylalanine ammonia lyase, activity remain unaltered after wounding. Reyes et al. [97] further verified that the effect of this stress depends on the type of vegetable. In sliced onions, wounding was found to increase phenolic content and antioxidant activity [17].

Given the distribution of onion flavonoids in the bulb tissues, the wounding effect is also affected by the cutting technology. Hence, generally, the outer leafs contain the highest flavonoid levels, whereas inner layers have the lowest amount of flavonoids [17, 98, 99]. The greatest loss was during preprocessing steps such as peeling and trimming. Keeping in mind that onion human consumption is limited to edible part, the brown outer leafs are not actually being under consideration. As referred, flavonoid distribution was described as not homogeneous in edible onion bulb. Hence, the initial flavonoid content and evolution could depend on the cutting technique. Overall, trending to increasing the initial flavonoid content was generally observed in chopped onion [17] and sliced onion [100]. However onions could be also cut into half onion rings, onion rings, diced onions, and julienne strips. Recent studies evaluated the effect of the type of cutting in the flavonoid contents [89]. They found that slicing led to greater anthocyanin content in comparison to dicing. Another controversy could be extracted from the research about how cutting affects onion flavonoid content. Temperature, light presence or absence, and storage time have normally been studied in parallel to cut effect. Some authors attribute the only effect of storage time [89], whereas other authors verified differences promoted by temperature changes [17]. Further studies are needed to verify the differences in the flavonoid evolution and their mechanisms depending on the tissue analyzed.

2.1.3.1.2. Sanitizing technologies

Different sanitizing technologies emerged in food science to disinfect fresh-cut food prior to package. Fresh-cut or minimally processed food has been described by the USDA and FDA like fruits and vegetables cut, washed, packaged, and further maintained under refrigeration conditions. Fresh-cut products are therefore raw. Even though minimally processed food remains in a fresh state, it could be physically altered from the original form. Fresh-cut food is ready to eat or cook, without freezing, thermal processing, or treatments with additives or preservatives [101]. Given the nature of fresh-cut products which are not subjected to thermal processing, it is necessary to include some sanitizing technologies to maintain the hygienic quality of the raw food. Washing is one of the most important processing operations and uses physical and chemical treatments to eliminate, or at least reduce, the population of pathogenic and spoilage-inducing microorganisms. However, according with Perez-Gregorio et al. [102], the main effect contributing to the loss of flavonols in fresh-cut onion slices is their solubility in immersion in water leading to losses from 17 to 23% of flavonoids at 4 or 50°C. Despite that sodium hypochlorite is not allowed as sanitizer of fresh-cut vegetables in some European countries, it is still the most used for being inexpensive and easy to use and for having a broad spectrum of activity [102]. Chlorine can oxidize organic matter in foods or in water, and in the latter case, by-products such haloforms and haloacetic acids, which are potentially carcinogenic and mutagenic, can be formed [103]. Searching for organic chlorinated products (sodium dichloroisocyanurate, potassium dichloroisocyanurate, dichloroisocyanuric acid, and trichloroisocyanuric acid) as alternative sanitizing agents gained interest in recent years [104]; nevertheless the antimicrobial efficacy in onions of these sanitizers was lower than the others like hydrogen peroxide [105]. It was verified that onion flavonoid content experienced a significantly decrease for chlorine, organic chlorine, or hydrogen peroxide treatment [102]. Alternative treatment like nisin and citric acid in combination was also tested as sanitizer in fresh-cut onion manufacturer. Nisin and citric acid are generally recognized as safe (GRAS) for use as food ingredients [106] which is an advantage in the use of nisin and citric acid in the microbial cleaning of fresh-cut onions. Cheng et al. [100] verified an increase of total phenolics and antioxidant activity after using niacin and citric acid to wash fresh-cut onions. It was therefore highlighted that it might be used as a safe preservative for fresh-cut onions, whereas the phenolic content will be improved. Among the chemical methods for controlling postharvest diseases, other treatments as UV-C irradiation were assayed. UV radiation in the range of 250–260 nm is lethal to most microorganisms, including bacteria, viruses, protozoa, mycelial fungi, yeasts, and algae and also leads to increase the onion flavonoid content [102]. Other treatments like ozone [107] were also used as sanitizer agent; however, no scientific paper has been found to evaluate the effect of this treatment in onion flavonoid content.

2.1.3.1.3. Packaging: atmosphere and package material

As already referred, fresh-cut technology could promote several physiological changes that could induce microbial spoilage. Furthermore, color changes, softening, surface dehydration, water loss, translucency, and off-flavor and off-odor development are other frequent causes of quality loss in fresh-cut products. The use of innovative modified atmospheres as well as edible coatings is nowadays standing out against revolutionary techniques to control the food safety; likewise the fresh state was maintained. Even though some studies have already demonstrated the effectiveness of these proceedings, more studies are required to better keep the minimally processed organoleptic properties. Moreover, further studies about how packaging might affect onion flavonoids are still required. Little scientific information is available to better know the effect of "ready-to-eat" packaging onion in its flavonoid content. Flavonoid stability was evaluated during fresh-cut onion storage in perforated films [108] or polyethylene and polyethylene terephthalate cups [17]. Overall, the onions experienced changes in flavonoid content during storage time. Storage conditions like light presence or absence, temperature, and storage time marked the onion flavonoid evolution. Hence, anthocyanins increase under light but experienced a decrease under dark storage conditions [17]. Moreover, the individual flavonoid stability was very different, the malonated anthocyanins being much more stable than the corresponding non-acylated pigments [108]. In addition, the arabinosides were shown to be less stable than the corresponding glucosides [108].

There is still a gap in the knowledge as how the package material affects the onion flavonoid evolution during storage time. It is also necessary to deepen the study of package atmosphere influence or what is the best type of package in order to maintain the levels of onion flavonoids.

2.1.3.2. Cooking: frying, microwaving, baking, and boiling

The impact of common domestic and technological treatments on flavonoid composition in onions was studied [23, 91–93, 109–111]. During technological and culinary treatments, important chemical and biochemical reactions occur in onion tissue. Such reactions may have an impact on the flavonoid structure, resulting in changes of the bioavailability and activity of these compounds [112]. In general, papers report that cooking of onions led to a decrease in total flavonol content, but these losses vary depending on the culinary treatment (frying, boiling, roasting, etc.) and on the length of exposure to this treatment. Overall, slight conditions did not affect to the flavonol content, but intense treatments cause flavonol losses from 16 to 30% [23]. Boiling onions led higher losses of quercetin glycosides, which leached to the boiling water until 53% in intense treatments [23]. Quercetin degradation was higher for diglucosides than monoglycosilated quercetin derivatives, whereas anthocyanins experienced the greater losses under cooking temperature exposure [23].

2.1.3.3. Frozen onion

In addition to ready-to-use vegetables, the trend to find a higher number of preprocessing vegetables is increasing in the commercial areas. The modern lifestyle drives to a high consumption not only in minimally processed food but also in frozen vegetables that are ready to cook and cheaper than fresh vegetables. Frozen storage has also an economic advantage for manufacturers since the wastage of unused products is reduced and the shelf life increases. However, the freezing process could affect the food quality, and this is a worrisome point for consumers. It is well known that frozen vegetables may have a lower nutritional value than their respective commodities. Little knowledge is highlighted about how this technology could affect to onion flavonoid content. However few authors concluded that frozen onions lead to an increase of onion flavonoid content [23, 113]. This could be a potent strategy to increase the consumption of frozen vegetables.

2.1.3.4. Dehydrating and freeze-dried onion powder

Industry often carries out processes based in the food water extraction such us freezing and drying to achieve the objective of long-term storage. However, the health-promoting ability and nutritional attributes of fruits and vegetables depend on the type of processing employed. Onions can be marketed as powder for cooking purposes after drying processes [114]. Drying technological developments are driven by consumer who demands for healthy, fresh-like, and convenient food. The trending in consumer demand has increased for processed products that are ready to use, cook, and eat but keeping more of their original characteristics. The development of operations that minimize the adverse effects of processing is therefore required by an industrial point of view. The main concern in food drying is related to a loss of volatiles and flavors, changes in color and texture, and a decrease in nutritional value associated with the process. Hence, the effect of dehydration on onion quality was studied [115]. Mass production of dried foods is often accomplished through the use of convective dryers. This drying process suffers from quality losses regarding color, flavor (taste and aroma), and texture, while rehydration is often poor. Freeze-drying process produces the highest-quality dried food product since the food structure is not damaged during sublimation. Nevertheless the freeze-dried process has a strong disadvantage, is much more expensive than convective drying, and is therefore only used for the production of a minor volume of high-value products.

Regardless of the drying procedure used, dried food has residual enzyme and microbial activities, essential parameters to extend the food shelf life. On the other hand, the minimization of enzymatic activity given by the dehydration process might also influence quality factors like antioxidant activity and flavonoid content. Hence, it was verified that onion flavonoid content increases after freeze-drying process [19].

In recent years, there has been an increasing interest of the food industry in incorporating ingredients with health beneficial properties. Among these ingredients, spices are recognized by their flavoring and coloring potential. Spices may contain phenolic compounds and contribute to the intake of natural antioxidants. Therefore, the incorporation of purified extracts of bioactive compounds in many foods may represent an interesting alternative to increase consumption of these substances and allow the population to benefit from the positive effects attributed to them. Onion, therefore, would be used as freeze-dried powder to improve the antioxidant capacity of foods, and onion flavor could be added.

Overall, further studies are needed in order to improve the knowledge about how onion flavonoids are affected by domestic or industrial treatments. The scientific evidences about flavonoid content could be modulated by normal industry processes and could be also profited to offer food with high quality and high added value.

2.2. Valorization of onion by-products

The production of onion worldwide increased by a 25% over the past 10 years, with a production of about 83 million tons nowadays [116], which makes onions as the second most important world horticultural crop after tomatoes. This high level of production gives as a result more than 500,000 tons of onion skin waste (OSW) which are discarded within the European Union every year [117]. Therefore, the resulting wastes and by-products have become a major problem [118]. They include onion skins, the outer two fleshy scales, and roots generated during industrial peeling but also undersized, malformed, or damaged onion bulbs. They are not suitable as fodder because of their strong characteristic aroma and neither as an organic fertilizer due to the rapid development of phytopathogenic agents such as *Sclerotium cepivorum* [119]. Their disposal commonly involves landfill with high economical costs and important environmental impact [120].

The recovery of valuable phytochemicals with high potential for the pharmaceutical, food, and cosmetics manufacturing is of key importance [121]. The onion waste has been identified as a potential source of flavor compounds, dietary fiber components, nonstructural carbohydrates like fructans and fructooligosaccharides, and flavonoids particularly quercetin glycosides [117, 122]. Most of the studies have been performed at a laboratory scale, so further research is necessary in order to scale up these processes to the industry requirements, assessing their economical viability. Onion composition is variable and depends on cultivar, stage of maturation, environment, agronomic conditions, storage time, and bulb section.

It is key to know the composition of each industrial onion waste to know its potential health benefits. Quercetin 4′-glucoside and quercetin 3,4′-diglucoside are in most cases reported as the main flavonols of the flesh, whereas onion skins contain higher concentrations of quercetin aglycon [123, 124]. There is a big potential opportunity given the increasing demand of consumers for substituting synthetic compounds by natural substances [125]. The presence of these flavonoids in onion products confers them some healthy properties. Flavonoids are shown to have antioxidant activity, free radical scavenging capacity, coronary heart disease prevention, and anticancer activity. Some flavonoids exhibit potential for antihuman immunodeficiency virus functions. Quercetin is known for its anticancer, anti-inflammatory, and antiviral activity [126]. Future investigations on the bioactivity, bioavailability, and toxicology of onion product phytochemicals [127] and their stability and interactions with other food ingredients [128] should be performed and carefully assessed by in vitro and in vivo studies. Functional foods represent an important, innovative, and rapidly growing part of the overall food market.

3. Future challenges for plant scientists and growers

This chapter deals about the current state of knowledge on the main factors affecting the flavonoid content in onions, as well as different approaches that can be applied to increase the accumulation of these compounds. For example, red cultivars contain the highest flavonoid levels; in this sense, also resistant onions present higher flavonoid levels than those that are susceptible. The nonedible dry skin is richer in flavonoids than the flesh, promoting the nonedible portions as a source of natural antioxidants. Within the edible bulb, a decrease across the onion from the outer onion scales to the inners is also found. With regard to soil management factors, the nitrogen fertilizer levels should be minimized to favor flavonoid levels. It was also found that organically grown onions present higher levels of flavonoids and antioxidant activity than conventional. Late lifting of onions generally results in higher concentrations of quercetin glucosides than early lifting.

Phenolic compounds can affect sensory attributes such as color, flavor, bitterness, and texture affecting the consumer assessment. The identification of specific compounds in different onion cultivars and agronomic practices would lead to a better understanding of the physiological responses to onion consumption [17–20, 23–25]. This would aid the development of onion production systems that provide an increased health benefit [56] and the development of guidelines for the consumption of these compounds. An interesting and challenging aspect for future research is to clarify the interactions between genotype and agro-environmental factors on the flavonoid composition in onions [129].

The production of fresh "functional food" with defined health claims may be favorable for a premium market segment. In the future, the minimum quality of plant foods could be defined on the base of their content of bioactive components [130]. One of the projects that have been awarded over the years is given below as an example of the fruit and vegetables research community [131] to generate successful applications in the calls published by the EU Commission: FLAVO is the project for "flavonoids in fruits and vegetables: their impact on food quality, nutrition and human health." The project is centered on fruits widely available to Europeans—apple, grape, and strawberry—together with their derivatives. FLAVO aimed to monitor the flavonoids in fruits and vegetables and to optimize their beneficial effects. This action was promoted by the European Fruit Research Institutes Network (EUFRIN), and a similar project would be desirable for the vegetable sector with the support of the European Vegetable Research Institutes Network (EUVRIN) to cover areas such as (a) the study of consumer behavior about new products, (b) selection of improved plant foods by breeding, (c) the

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choice of agronomic techniques to maximize flavonoids, (d) knowledge on the appropriate dose of flavonoids for beneficial effects, and (e) the dissemination of the results to consumers and other stakeholders.

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