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Review

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Effect of storage, food processing and novel extraction technologies on onions flavonoid content: A review

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Abstract

Onions play an important part in the daily diet for most populations around the world owing to their nutritional composition and their unique capacity to naturally flavor dishes. Onions contain quercetin and its derivatives - the predominant flavonoid in onions that exert a great contribution to the effective bioactive properties of onion, including its derived products. The present paper comprehensively reviewed flavonoids (with a specific focus on quercetin in onions): their chemical composition, distribution, bioactivities of onion, and factors including a particular focus on how they can be affected by various post-harvest conditions (storage and food processing). In addition, research on the extraction of flavonoid compounds from onions using a number of novel technologies was also reviewed.

Keywords: Onions; Quercetin; Bioactivity of flavonoids; Storage; Post-harvest processing; Innovative extraction techniques

1. Introduction

The onion (*Allium cepa* L.) originated in central Asia and is one of the oldest cultivated plants, with cultivation records dating back to more than 4000 years. It is the second most cultivated vegetable grown worldwide, with an estimated total production around 66 to 85.7 million tons per year. It is commercially grown in more than 170 countries (Bahram-Parvar & Lim 2017 Prokopov et al., 2017; Petropoulos, Ntatsi, & Ferreira, 2017; Campone et al., 2018). During the last decade, the production has increased by over a quarter of the total production (Sharma, Mahato, & Lee 2018). Onion is a member of the family Amaryllidaceae and the genus *Allium*. *Alliums* are frequently known as a perennial plant, which has bulbous and underground stems. Its close relatives include garlic, chives, leeks, and a non-edible species only with flowers (Bernaert, De Clercq, Van Bockstaele, De Loose, & Van Droogenbroeck, 2013; García-Herrera et al., 2014; Liguori et al., 2017; Sidhu, Ali, Al-Rashdan, & Ahmed, 2019). There are generally three color varieties of onion (red, yellow/brown and white) with distinct flavors (Ferioli, & D'Antuono, 2016; Bahram-Parvar & Lim, 2018), ranging from mildly sweet to very strong. As a food, onions can be served as cooked (e.g. stir-fried, dried, or roasted), or raw (flavor salads or dips) (Arshad et al., 2017).

Fresh onions can be directly supplied to the market, or further processed into different forms, for example, dried powders or flakes (Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2011a; Khan, Ansar, Nazir, & Maan, 2016; Choi, Lee, Kim, & Lim, 2017; Prokopov et al., 2018; Edith, Mang, Abound, & Nicolas, 2019; Piechowiak, Grzelak-Błaszczyk, Bonikowski, & Balawejder, 2020). Storage and processing as post-harvest treatments may change onions' chemical structure of bioactive compounds that can lead to profound differences in bioavailability (Hithamani, Kizhakayil, & Srinivasan, 2017; Zudaire et al., 2017; Sans et al., 2019). Previous studies on the effect of storage conditions such as temperature, time, freeze-drying, and packaging on flavonoids have been evaluated (Islek, Nilufer-Erdil, & Knuthsen, 2015; Majid & Nanda, 2017; Petropoulos, Ntatsi, & Ferreira, 2017; Zudaire et al., 2017). Growing international markets for onion products aimed to develop dehydrated methods such as powder or canned onions to reduce product loss during storage (Arslan & Özcan, 2010; Edith et al., 2018; Sehrawat & Nema, 2018). Additionally, dehydrated products possess medicinal features, for containing higher concentrations of beneficial compounds than fresh onions (Mitra, Shrivastava, & Rao, 2012; Sharma et al., 2015a; Chemat et al., 2017; Michalak-Majewska, Sołowiej, & SłAwińska, 2017; Seifu, Tola, Mohammed, & Astatkie, 2018).

The change of onion flavonoids with domestic treatments such as slicing chopping, shredding, peeling (Berno, Tezotto-Uliana, dos Santos Dias, & Kluge, 2014; Islek, Nilufer-Erdil, & Knuthsen, 2015; Ifie & Marshall, 2018), cooking (Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009; Harris, Brunton, Tiwari, & Cummins, 2015), or frozen (Pérez-Gregorio, Regueiro, González-Barreiro, Rial-Otero, & Simal-Gándara, 2011b) were also investigated by a number of studies. Furthermore, onions could be also industrially processed. Industrial processing not only includes all domestic treatments but also includes thermal processing (roasting or boiling) and non-thermal processing (high pressure and ultraviolet).

However, some food ingredients are sensitive thermally and vulnerable to chemical or physical changes. These methods cause losses of nutritional compounds and can be energy and time consuming as well. In order to advance the above conventional processing technologies, more 'green and innovative' processing techniques such as microwave processing and ultrasound-assisted processing, are getting more attention in extracting beneficial bioactive compounds (e.g. flavonoids).

This paper reviews recent key studies regarding the main factors and approaches affecting the flavonoid content in onions during post-harvest (i.e. storage conditions, thermal and non-thermal processes, and extraction treatments). This review with a perspective of post-harvest conditions in relation to the accumulation of flavonoids provides a more comprehensive study of onions.

2. Main components of phenolics in onions

Flavonoids are a class of secondary metabolites; a natural substance with a number of different phenolic structures, which are widely distributed in fruits, vegetables and some certain beverages (Panche, Diwan, & Chandra, 2016). They are characterized as important antioxidants due to their high redox potential, which allows them to act as reducing agents and singlet oxygen quenchers (Tsao & Yang, 2003).

Flavonoids are one of the most important polyphenols and more than 4000 flavonoids have been identified among over 9000 phenolic compounds in plants (Ignat, Volf, & Popa, 2011; Pérez-Gregorio, Regueiro, Simal-Gándara, Rodrigues, & Almeida, 2014). Flavonoids are low molecular weight compounds, consisting of fifteen carbon atoms, in a form of C_6–C_3–C_6 configuration. Their structure is consists of two phenyl rings (ring A and B), connecting by a three-carbon bridge and becoming a six-membered oxygenated heterocycle (ring C) (Fig 1 A). Most flavonoids are presented as glycosides and other conjugates. It means that they have a complex nature of having a large number of different molecules. Different categorizations of flavonoids can be determined by oxidation degree, annularity of ring C, and connection position of ring B, for example flavonols, flavones, flavanols, flavanones, isoflavones, and anthocyanidins (Fig 1 B) (Table 1) (Ignat, Volf, & Popa, 2011; Kumar & Pandey, 2013). In addition, substitutions to rings A and B can also lead to different compounds within each class of flavonoids (Ignat, Volf, & Popa, 2011). Many studies have investigated the presence of flavonoids in onions (Pérez-Gregorio, García-Falcón, Simal-Gándara, Rodrigues, & Almeida, 2010; Arshad et al., 2017). Flavonoid levels in the edible portions of onions range from 0.03 to 1 g/kg while onion skins contain significantly higher levels of flavonoids of 2–10 g/kg (Sharma, Mahato, Nile, Lee, & Lee, 2016; Akdeniz, Sumnu, & Sahin, 2018).

2.1. Flavonols

Flavonols are a main type of flavonoids in onions and they are consist of quercetin (3,5,7,3′,4′- pentahydroxyflavone). In addition to quercetin, relatively fewer flavonols are consist of kaempferol, isorhamnetin, and myricetin with their derivatives (Panche, Diwan, & Chandra, 2016). Flavonols are the most abundant glycosides in onions with 250mg/kg, which are higher than broccoli (100mg/kg) or apple (50mg/kg) (Liguori et al., 2017). Moreover, they are found to be associated with many health-promoting benefits such as antioxidant capacity and reduced risk of vascular disease (Panche, Diwan, & Chandra, 2016).

In total, minimal 25 different flavonols have been identified in onions, and quercetin derivatives are the most important ones in all onion cultivars (Slimestad, Fossen, & Vagen, 2007). The glycosyl units of quercetin derivatives have been identified as glucose in most cases. They are attached to the 4', 3, and/or 7-positions of the aglycones (Fig 1 C). Quercetin 4'glucoside and quercetin 3,4' diglucoside are known to be the main flavonols in previous studies. Quercetin diglucoside and monoglucoside account for up to 93% of the total flavonol content in onions (Lombard, Geoffriau, & Peffley, 2002). Sellappan and Akoh (2002) also reported that quercetin is the major flavonoid found in onions, present in the conjugated form, quercetin 4' glucoside (Q 4' G), quercetin 3,4' diglucoside (Q 3,4' D), and quercetin (Q). Slimestad, Fossen, and Vagen (2007) also agreed that quercetin and its derivatives were the most dominant flavonols found in studied onion cultivars. Similarly, Lombard, Peffley, Geoffriau, Thompson, and Herring (2005) also reported that Q 4' G and Q 3,4' D are the main flavonols present in onions, accounting for about 80 to 95% of the total flavonol content. Quercetin levels, to some extent, represent the flavonol compounds present in onions. Quercetin is essential to human. It can be found in various fruits and vegetables, particularly abundant in onions (0.3 mg/g fresh weight) (Mojzer et al., 2016). Quercetin, its glycosides, and oxidative products are significant antioxidants and play important roles in the oxidative stress process (Bystrická, Musilová, Vollmannová, Timoracká, & Kavalcová, 2013).

2.2. Anthocyanins

Anthocyanins are a type of flavonoids and they can generally be found in plant cells mostly in flowers and fruits, but also in leaves, stems, and roots. They give color to their plants since they are water-soluble vacuolar pigments that may appear as red, purple, or blue depending on pH values. Even though anthocyanins do not constitute a major flavonoid content in onions, they have frequently been reported to be presented in red onions. Anthocyanins are mainly presented in red onions (250mg/kg). (Liguori et al., 2017). The red varieties of onions do not only have the highest content of flavonols, but they also contain red anthocyanins in the form of glycosides of cyanidin, peonidin, and pelargonidin (Bystricka et al., 2013). Slimestad, Fossen, and Vagen (2007) reported that there are at least 25 different anthocyanins in red onions, with the content of anthocyanins in some red onions has been reported to be approximately 10% of the total flavonoid content (Slimestad et al., 2007; Lee, Patil, & Yoo, 2015). The anthocyanidins (or aglycons) are an aromatic ring A connected to a heterocyclic ring C that contains oxygen, which is also connected by a carbon-carbon bond to a third aromatic ring B (Table 1).

3. Bioactivity of flavonoids in onions and human health

Flavonoid compounds are known for their ability to provide a defense against the oxidative stress of oxidizing agents and free-radicals (Russo, Spagnuolo, Tedesco, Bilotto, & Russo, 2012; Beretta et al., 2017; Assefa et al., 2018; Wang, Li, & Bi, 2018). They are widely recognized for their health benefits, which include; antioxidant, anti-inflammatory, antimicrobial and anticancer bioactivities (Tiwari & Cummins, 2013; Sharma, Mahato, & Lee, 2018; Quecan, Rivera, Hassimotto, Almeida, & Pinto, 2019) and their protective effects against different degenerative pathologies such as; cardiovascular and neurological diseases, and other dysfunctions based on oxidative stress (Wang, Li, & Bi, 2018). Flavonoids have been shown to present antioxidant, anti-inflammatory, anti-proliferative, anti-tumor activities and have been associated with a reduction in the incidence of diseases such as cancer and heart disease (Paredes-López, Cervantes-Ceja, Vigna-Pérez, & Hernández-Pérez, 2010; Ren et al., 2017). Flavonoids are important antioxidants due to their high redox potential, thereby allowing them to act as reducing agents (hydrogen donors) (Tsao & Yang, 2003).

Additionally, anthocyanins not only have strong biological functions such as anti-inflammatory and antioxidant activities, which are linked to the prevention of a number of degenerative diseases but also provide sources of natural food dyes (Bleve et al., 2008).

Quercetin occurs at high levels in onions (Tiwari & Cummins, 2013). It is an effective scavenger of free radicals and is also associated with antiviral, anti-inflammatory, antibacterial and muscle-relaxing properties (Russo, Spagnuolo, Tedesco, Bilotto, & Russo, 2012). The same authors reported that there was substantial evidence demonstrating the chemo-preventive properties of quercetin against certain types of cancers, including; breast, colon, stomach, intestinal and lung (Harris, Brunton, Tiwari, & Cummins, 2015).

The daily intake of quercetin in the human diet has been estimated to be about 5-40 mg/day (Mojzer, Hrnčič, Škerget, Knez, & Bren, 2016). If individuals who consume high quantities of onions in a day, the intake of quercetin can go up to 200-500 mg/day (Harwood et al., 2007). It shows that onion contains a high level of quercetin that can be absorbed by the human body.

With regard to quercetin bioavailability in humans, it was concluded that the glycosides of quercetin (52%) are more efficiently absorbed than quercetin itself (24%) (Williamson, Kay, & Crozier, 2018) and sugar residues in the glycosides influence the extent of absorption. Onions that contain glucosides are better sources of bioavailable quercetin (Mojzer, Hrnčič, Škerget, Knez, & Bren, 2016; Williamson, Kay, & Crozier, 2018). It is suggested that glucosides of quercetin can be used to assess the bioavailability by using cell lines, such as Caco-2 cell cultures model and mimic human digestion to fast approach to address flavonoid absorption. Although it has been nearly a decade since the bioavailability of onion flavonols were studied, there have been few subsequent new developments and breakthroughs.

3.1. Bioactivity in onion by-products

There is a large amount of industrial onion wastage that has been reported as a great concern (Roldán, Sánchez-Moreno, de Ancos, & Cano, 2008; Singh, Krishan & Shri, 2017; Prokopov et al., 2018). Since onions are important both commercially and medicinally, the large amount of onion waste (e.g. 450,000 tons of onion waste is generated annually in European Union) should be proper managed (Singh, Krishan & Shri, 2017). The onion waste (i.e. non-edible dry skin, the outer two fleshy leaves and the top and bottom bulbs), therefore, has been identified as a potential source of flavonoids particularly quercetin glycosides (Roldán, Sánchez-Moreno, de Arcos, & Cano, 2008; Burri, Ekholm, Håkansson, Tornberg, &

Rumpunen, 2017; Nile, Nile, Keum, & Sharma, 2017; Campone et al., 2018). On the other hand, the onion wastes (surpluses and residues of onions) can be processed and reused as bioactive food ingredients. It is well known that onion and its by-products possess many medical characteristics such as anti-inflammatory, antioxidant, and antibacterial, which can prevent certain illnesses to a great extent (Roldán, Sánchez-Moreno, de Ancos, & Cano, 2008; Singh, Krishan, & Shri, 2017).

4. Post-harvest storage factors and approaches in the accumulation of flavonoids in onions

Storage conditions are essential to maintain high-quality onions and its by-products since the high instability of flavonoid compounds can be easily changed during storage (Tiwari & Cummins, 2013; Sharma, Asnin, Ko, Lee, & Park, 2015b; Petropoulos et al., 2016; Murkute & Gorrepati, 2018) Storage conditions, such as storage temperature, time or storage technologies impact the synthesis, retention, or breakdown of flavonoids (Tiwari & Cummins, 2013; Sharma, Assefa, Ko, Lee, & Park, 2015c).

4.1. Effect of temperature and time on flavonoid compounds during storage

The effect of storage temperature on flavonoid compounds in onions has been investigated by a number of researchers. Yoo, Lee, and Patil (2013) reported that storage at 30 ^{o}C resulted in an increase of quercetin glucoside by about 50% after five months of storage. They did not observe significant changes in quercetin glucosides when bulbs were stored under controlled atmosphere (4 ^{o}C with 1% O_2 and 99% N_2). With a higher temperature, ethylene was accumulated more during storage which can stimulate the activity of Phenylalanine ammonia-lyase (PAL), a key enzyme in the biosynthesis of phenolic compounds and accumulation of phenolic constituents (Benkeblia, 2000; Leja, Mareczeka, & Benb, 2003). This is also evident in Rodrigues, Pérez-Gregorio, García-Falcón, Simal-Gándara, and Almeida's study (2010) where a significant increase in flavonols was observed during storage due to the effect of PAL. On the other hand, cold storage contributes to the effect of flavonoid compounds in onions (Mogren, Olsson, & Gertsson, 2007). Swedish onions showed a slight decrease in QG during storage at 1 ^{o}C (Mogren, Olsson, & Gertsson, 2007), while Polish onions stored at 1 ^{o}C maintained a stable QG level (Grzelak, Milala, Król, Adamicki, & Badełek, 2009). The level of Q 4' G did not show any consistent changes, while Q 3,4' D increased by 30-51% during eight months of storage at 2 ^{o}C (Olsson, Gustavsson, & Vagen, 2010). The reason that flavonoids could remain at the same level or increase during storage is because although most physiological and enzymatic activities were delayed under cold storage, a succession of chemical composition change was triggered by high respiration rates of bulb tissues and sprouting, result in an increase in quercetin and quercetin glycoside contents (Sharma, Assefa, Kim, Ko, & Park, 2014; Majid, Dhatt, Sharma, Nayik, & Nanda, 2016; Majid & Nanda, 2017). Furthermore, Gennaro et al. (2002) investigated the effect of cold storage on total anthocyanins, and reported a total decrease of anthocyanins in red onions during the storage, with higher levels of loss of anthocyanins at 2 ^{o}C, which seems to indicate that flavonol glucosides are more stable than anthocyanins during cold storage.

All the aforementioned studies of cold storage of onions were above 0 ^{o}C. Pinho et al. (2015) reported that domestic freezing (below 0 ^{o}C) onions portions can extend onions shelf life and can be a good alternative to prevent the loss of unused fresh onions. Although little has been known on how this technology could affect onion flavonoid content, few authors concluded that frozen onions lead to an increase of onion flavonoid content (Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009; Pinho et al. 2015). Pinho et al. (2015) evaluated the evolution of flavonoids of two Portuguese onion cultivars (Branca da Póvoa, white; and Vermelha da Póvoa, red) during storage below 0 ^{o}C, simulating domestically freezing conditions (–18 ^{o}C). Frozen portions of onions with different periods of domestic storage (3-5 months) at ambient temperature resulted in increased flavonoid content when compared with the ones before freezing (portions from the same onions at room temperature). These results suggested that frozen storage of onions pieces positively affected flavonols. From the above discussions, it can be concluded that storage temperature can influence the stability of flavonoids in onions considerably. Storage at low temperatures leads to the best preservation of the flavonoids present in the onion (Berno, Tezotto-Uliana, dos Santos Dias, & Kluge, 2014; Petropoulos, Ntatsi, & Ferreira, 2017).

4.2. Storage technologies

Besides temperature and time factors, many other storage technologies are employed to prolong onions or its product shelf life (Berno, Tezotto-Uliana, dos Santos Dias, & Kluge, 2014; Zudaire et al., 2017). Some studies have been carried out to investigate the effects of these technologies on the levels of flavonoid compounds in onions during storage. In this paper, freeze-drying and packaging as the main technologies for onion storage are reviewed.

4.2.1. Freeze-drying

Onion is often processed and marketed as dried powders for culinary uses and for its long-term storage (Alezandro, Lui, Lajolo, & Genovese, 2011; Mitra, Shrivastava, & Rao, 2012; Ren et al., 2018a). Pérez-Gregorio, Regueiro, González-Barreiro, Rial-Otero, & Simal-Gándara (2011b) studied flavonoids content of onions after freeze-drying and found that the process of freeze-drying increases flavonoids and anthocyanins in onions by 32% and 25% respectively. Freeze-drying technology brings structural changes in onion tissues which make flavonoids more available and accessible. They further indicated that freeze-dried onions kept in air-tight containers and stored in dark conditions at room temperature for six months showed no significant quality loss in flavonoids. Freeze-dried onions after long-term storage could potentially inactivate various enzymes and ethylene in onions, resulting in the stability of flavonoids (Rodrigues, Pérez-Gregorio, García-Falcón, Simal-Gándara, & Almeida, 2010). Freeze-drying as a new technology is recommended during storage, which can be applied in the food industry for better retention of bioactive compounds.

4.2.2. Packaging

The type of package could be important for preserving fresh-cut onion slices' quality during storage. Flavonoid stability was evaluated in the fresh-cut onion during storage packaging in vacuum or closed cups of polyethylene terephthalate (PET) and polystyrene (PS) (Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2011a). They reported that an increase of flavonols was observed in transparent PS with light conditions and it could be explained by the increased ethylene activity and PAL activity. In addition, it is also necessary to investigate the influence of the package atmosphere for maintaining onion flavonoids. Islek, Nilufer-Erdil, and Knuthsen (2015) studied the effect of atmospheric conditions on flavonoids change in sliced and fried onions during storage. They found that sliced onion packed in a vacuum in dark conditions at +5 ^oC and −18 ^oC for 21 days preserved better flavonoids content while fried onion packed in a vacuum in dark at +5 ^oC for 7 days obtained the highest flavonoids. In addition, Marta et al. (2013) reported two different package systems for onion storage to improve quality of onion: the normal atmospheres (NA) and controlled atmosphere (CA) of the 4 compositions: (1) 5% CO_2 + 5% O_2, (2) 5% CO_2 + 2% O_2, (3) 2% CO_2 + 5% O_2, (4) 2% CO_2 + 2% O_2. The authors concluded that the highest amounts of flavonoids in onions after storage are at the gas composition of 5% CO_2 + 5% O_2 under the CA package system.

Although controlled atmospheres used in packaging could increase the flavonoids content and storage life of onion bulbs, the application of this technique is questionable due to its high cost and the requirement of advanced facilities.

5. Post-harvest processing factors and approaches to flavonoids compounds

In recent years, various minimal food processing (peeling, chopping, and slicing) and thermal processes (boiling and frying) on the flavonoids from onions were evaluated. Different processing processes cause chemical and biochemical reactions in onion tissues, which may have an impact on the flavonoid structure, resulting in changes in the bioavailability and activity of these compounds (Schieber, 2017; Sans et al., 2019). In general, cooking could lead to a decrease in total flavonol contents in onions (Sans et al., 2019), but these losses vary depending on the treatment conditions (Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009). However, in some circumstances, flavonoids in onion bulbs are resistant to degradation during some normal processing operations.

5.1. Minimal food processing

Processing is expected to affect content, activity, and availability of bioactive compounds. Many minimal food processes like peeling, chopping, slicing, pressing, and sieving of foods were studied for the change of flavonoids (Ioannou, Hafsa, Hamdi, Charbonnel, & Ghoul, 2012; Berno, Tezotto-Uliana, dos Santos Dias, & Kluge, 2014). Table 2 showed some research on the effects of different minimal food processing on flavonoids and quercetins in onions. Ewald, Fjelkner-Modig, Johansson, Sjöholm, and Åkesson (1999) pointed out that major losses of flavonoids took place during the pre-processing steps when parts of the product were removed, for example, onion trimming can result in 39% flavonoids loss and a 21% loss of total quercetin glucoside was found in peeled onions (Gennaro et al., 2002). Similar results were shown by Makris and Rossiter (2001) who found a loss of flavonol content ranging from 10.7% to 17.7% during prolonged maceration (5 h) of the onion bulb. Hence, the flavonoid content could depend on the cutting technique.

In some cases, cutting increased flavonol content in onions. Overall, it was generally observed in chopped onions (Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2011a) and sliced onions (Chen, Hu, Zhang, Jiang, & Zou, 2016). This could be caused by the fact that wounding enhances flavonol biosynthesis through the induction of PAL to fight pathogen attack after tissue wounding (Tudela, Cantos, Espín, Tomás-Barberán, & Gil, 2002).

The above studies showed differences between various minimal processing methods and flavonoids in onions. Based on these findings, it can be suggested that chopping and slicing can be used as the most preferable cooking treatments since they could increase flavonol content in fresh-cut onions while trimming and maceration could be the least efficient ones.

5.2. Thermal processing

Heating can result in oxidation, thermal degradation, and leaching of bioactive compounds of fresh vegetables (Tiwari & Cummins, 2013). Different heating conditions (e.g., heating duration and temperatures) have different effects on the stability of quercetins in onions (Tiwari & Cummins, 2013; Ahmed & Eun, 2017). Both losses and gains in flavonoid compounds after heat treatment of onions have been reported by many researchers (Makris & Rossiter, 2001; Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009; Islek, Nilufer-Erdil, &

Knuthsen, 2015; Juániz et al., 2016; Ren et al., 2018b). It is believed that during thermal treatments, important chemical and biochemical reactions occur in onion tissues. In general, studies showed that cooking of onions led to a decrease of total flavonol content, but these losses vary depending on the thermal treatment (boiling, frying, microwave heating, and roasting, etc.) and the length of this thermal treatment, which could significantly degrade quercetin contents in onions (Juániz et al., 2016; Ren et al., 2018b). Table 3 lists the results of the variation of flavonoids and quercetins in onions after some thermal processing.

Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009) reported that moderate microwave heating (450 W for 4 mins) did not affect flavonol contents, but intense microwave (750 W for 4 mins) treatment caused flavonol losses of 16% and 18% for Q 3,4' D and Q 4' G, respectively. Although Lee et al. (2008) also found that quercetin levels decreased 4% after microwave cooking of onions, they did not take into consideration of power. In contrast, Ioku et al. (2001) and Ahmed and Eun (2017) revealed that microwave without water was more favorable for the retention of quercetins in onion tissues.

Lee et al. (2008) reported that frying (180 ^{o}C) decreased onion quercetin content by 25% to 33%. Similarly, Price, Bacon, and Rhodes (1997) showed that 15 mins frying (180 ^{o}C) reduced levels of quercetin conjugates by 23% to 29%. Ewald, Fjelkner-Modig, Johansson, Sjöholm, and Åkesson (1999) also found that frying (180 ^{o}C) for 5 mins in butter and rapeseed oil resulted in 24% and 39% losses of quercetin in onions, respectively. However, Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009) pointed out that frying with olive oil did not change the total levels of Q 3,4' D and Q 4' G. In a recent study conducted by Juániz et al. (2016), suggesting that onions frying in olive oil, frying in sunflower oil, and griddled increased the concentration of flavonoid compounds in the onions. This may be because the thermal destruction of cell walls and sub cellular compartments during the cooking process can release these compounds of onions. Griddle requires a higher temperature in comparison with the frying, and hence it showed the highest amount of flavonoid compounds, by 57.35% compared to raw onions. A similar effect has been found in baking where quercetin glucosides in onions increased (Lombard, Peffley, Geoffriau, Thompson, & Herring, 2005).

Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009) found that oven roasting (180 ^{o}C) without water did not change the total levels of Q 3,4’ D and Q 4’ G. Rohn et al. (2007), on the other hand, observed that onions roasting for 60 mins at 180 ^{o}C led to removal of sugar moiety resulting in the formation of Q 3,4’ D and Q 4’ G. They suggested that the sugar moiety attached at 3-position was more susceptible to thermal degradation compared to the sugar moiety attached at 4-position.

Boiling in water (100 ^{o}C) could cause a great loss of quercetins in onions as water-soluble quercetins would migrate into cooking water during the boiling procedure (Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009). Moreover, the level of quercetins in onions would decrease significantly with boiling time (Rodrigues, Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2009). Boiling onions for 30 mins led to losses of quercetin glycosides, during which 37% Q 3,4’ D and 29% Q 4’ G leached to the boiling water without being degraded. A reduction of about 53% and 44% of Q 3,4’ D and Q 4’ G were reported during 60 mins of boiling onions. Lombard, Peffley, Geoffriau, Thompson, and Herring (2005) also reported 18%

– 75% quercetin losses in onions boiled for 3 to 60 mins. Even though boiling onions would cause leach of the compounds, treating fresh-cut onion slices with hot water (60 ^{o}C) for one minute resulted in higher total flavonoids comparing to samples with no heat treatment applied (Siddiq, Roidoung, Sogi, & Dolan, 2013).

As reviewed in the literature, the differences among these thermal processes are mainly attributed to the exposure time and processing temperatures. It is acknowledged that in general, thermal processes could lead to a decrease of flavonoid content in onions due to the thermal degradation. However, in recent studies, it is also suggested that some thermal processing methods such as frying for a short time, could increase the level of these compounds. It is because the thermal processing kills vegetative microorganisms or inactivates enzymes, hence a higher level of flavonoids retained. Overall, the time and temperature of the processing, to a great extent, determine the amount of flavonoids loss.

5.3. Non-thermal processes

In addition to the thermal processes reviewed above, this section demonstrates the effect of different non-thermal processes on the retention of flavonoids. The non-thermal process has been recommended and applied to avoid loss of flavonoid compounds during thermal processing applications.

5.3.1. Ultraviolet (UV)

UV irradiation is currently used as a post-harvest treatment for sterilization, to inhibit sprouting and delay maturity (Higashio, Hirokane, Sato, Tokuda, & Uragami, 2007; Song et al., 2015; Liu, Hu, Jiang, & Xi, 2018). The UV radiation in the range of 250–260 nm is lethal to most microorganisms, including bacteria and viruses and it can be used to reduce the incidence of spoilage molds. Meanwhile, it also leads to an increase in the onion flavonoid content (Higashio, Hirokane, Sato, Tokuda, & Uragami, 2005; Pérez-Gregorio, González-Barreiro, Rial-Otero, & Simal-Gándara, 2011c). Rodov, Tietel, Vinokur, Horev, and Eshel (2010) found an increase in flavonol content of peeled onions treated with low (1.2 KJ/m^2) and medium (6.0 KJ/m^2) UV doses but a decrease in quercetin with high does (12 KJ/m^2).

5.3.2. High pressure

High pressure is more cost-efficient and environment-friendly with beneficial effects on bioactive compounds than other non-thermal processes (Vikram, Ramesh, & Prapulla, 2005; Yi et al., 2017; Dos Santos et al., 2018). Roldán-Marín, Sánchez-Moreno, Lloría, de Ancos, and Cano (2009) investigated the effects of high pressures (100–400 MPa) at (5-50 ^{o}C) for 5 mins on levels of flavonols content of onions. It showed that processing onion at 400 MPa/5 ^{o}C could increase flavonol by 33% higher compared to untreated onions.

5.3.3. Chemical solutions of onions

Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009) reported that ethylene treatments significant increase the flavonol content of the edible portion of onions. Ethylene can stimulate the activity of PAL, a key enzyme in the biosynthesis of flavonoid compounds (Pérez-Gregorio, García-Falcón, & Simal-Gándara, 2011a), which is in response to biotic and abiotic stresses (Naoumkina et al., 2010; Berno, Tezotto-Uliana, dos Santos Dias, & Kluge, 2014).

5.3.4. Encapsulation

Encapsulation is an efficient way to protect unstable compounds such as flavonoids and to change their unpleasant taste. It is important to use different coating materials to encapsulate phenolic compounds from onion skins to protect these compounds from environmental pressures. Capsules that obtained are suggested to be used in thermal processed foods such as baked and fried onions due to their high ability to against heat. In particular, the phenolic containing capsules can be combined with different food matrix (Akdeniz, Sumnu, & Sahin, 2018).

Non-thermal processes were used less frequently than thermal processes in both research and industry, despite that the former achieves a better result in flavonoids retention. Some limitations in non-thermal processes, for example, high-pressure technology include expensive equipment and little effect on food enzyme activity. For UV irradiation, there is, generally, a poor consumer understanding and a high capital cost. Due to these drawbacks, many companies are less willing to apply non-thermal technologies. It seems that there is still a long way to put novel methods into practical use. It is suggested that future studies could continue to optimize the production process and reduce the cost of non-thermal processes.

6. Extraction of flavonoid compounds from onion and its by-products

Onions are a good source of flavonoid compounds, in particular, quercetin and its derivatives. The extraction of these compounds has been explored in a number of studies (Santas, Almajano, & Carbo, 2010; Sharma, Mahato, Nile, Lee, & Lee, 2016; Singh, Krishan, & Shri, 2017). On the other hand, Sharma, Asnin, Ko, Lee, and Park (2014) suggested possible uses of sprouted and decayed onions as a source of quercetin and its glucosides. They further explained that during post-storage, sprouted and decayed onions occurred in post-storage are usually unappealing to consumers and hence dumped as waste, however, during this period, there is an increase in the content of quercetin and its glucosides. Food-processing industry has further suggested the exploitation of onion waste as a food ingredient (Roldán, Sánchez-Moreno, de Ancos, & Cano, 2008; Viera et al., 2017), due to its associated health benefits (Manousaki, Jancheva, Grigorakis, & Makris, 2016; Singh, Krishan, & Shri, 2017).

The conventional way to extract flavonoids from plant material is SLE (solid-liquid extraction) using organic solvents such as ethanol and methanol, either pure or mixed with water, although ethyl acetate, acetone, and hexane have also been used to extract the compounds from the solid materials into the liquid solvents (Makris & Kefalas, 2015; Singh, Krishan, & Shri, 2017). Nevertheless, the use of organic solvents can be harmful to the environment and for the persons working with them (Adekunte, Tiwari, Cullen, Scannell, &

O'Donnell, 2010). In addition, those conventional methods could result in the degradation of some chemically sensitive phenols due to intensive mechanical disruption. In addition, the involvement of long extraction periods, severe heating and extensive use of organic solvents in the conventional extraction methods could lead to the release of oxidative enzymes that promote degradation (Zill-e-Human et al., 2011; Singh, Krishan, & Shri, 2017).

Due to the possible downsides of conventional extraction methods, the use of new extraction techniques has increased in recent years, such as pressurized liquid extraction (PLE), pressurised hot water extraction (PHWE), microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE) and subcritical water extraction (SWE) (Kumar, Smita, Kumar, Cumbal, & Rosero, 2014; Campone et al., 2018; Khan et al., 2018). Table 4 lists the novel methods that have been used in the extraction of flavonoid compounds from onions. These novel methods are advantageous in comparison with conventional methods as the former requires shorter extraction periods and less organic solvents (Manohar, Xue, Murayyan, Neethirajan, & Shi, 2017; Liu, Zeng, & Ngadi, 2018). In the following paragraphs, several popular novel extraction methods were reviewed in detail.

PLE has been used as a novel method for the extraction of flavonoids from onions in a few studies (Søltoft, Christensen, Nielsen, & Knuthsen, 2009). It shows several advantages: simultaneous extraction, highly automated, use of small amounts of solvents, producing the cleanest extracts. On the other hand, it can be very time-consuming.

PHWE is an extraction technique that uses liquid water as an extraction solvent at temperatures above the atmospheric boiling point of water (100 ^{o}C /273 K, 0.1 MPa), but below the critical point of water (374 ^{o}C /647 K, 22.1 MPa). PHWE has been frequently used to extract higher levels of quercetins from onions (Lindahl et al., 2010; Liu, Sandahl, Sjöberg, & Turner, 2014). Furthermore, Lindahl, Liu, Khan, Karlsson, and Turner (2013) combined PHWE and enzymatic hydrolysis methods to exploit a continuous way of extraction of quercetin from onions. The optimized combined method achieved a slightly higher extraction yield of quercetin within a much shorter period of time. Compared to conventional extraction with acid-catalyzed hydrolysis, the new method is more accurate. The continuous method combined extraction with hydrolysis greatly reduced laboratory work. Although degradation of flavonoids is minimized in PHWE, it encounters potential commercial and technical drawbacks especially PHWE-EEH, which contains a high ratio of the enzyme. The cost of enzymes could be expensive and hence it is not preferable in large industrial-scale production.

As one of the most effective extraction methods, a number of researchers employed ultrasound processing either on its own or in the combination with heat or pressure for onion extractions (e.g. Nowacka & Wedzik, 2016; Ren et al., 2018c; Zudaire et al., 2018). It is evident that ultrasound processing requires shorter processing time, but achieve higher throughput with lower energy consumption. More specifically, Chemat, Zill-e-Huma, and Khan (2011) reported that ultrasound-assisted extraction led to a yield of gallic acid equivalents total phenolic content (TPC) of 121±3.8 mg GAE/g dry weight, over 20% more than the yield by conventional maceration method (89.6 ± 2.3 mg GAE/g dry weight) in 30 mins of extraction.

Zill-e-Huma, Abert-Vian, Mangonnat, and Chemat (2009, 2011) and Pal and Jadeja (2019) used a green technology - microwave to assist the extraction of flavonoids from onions, suggesting that microwaves accelerated the diffusion of secondary metabolites by increasing tissue softness and cell permeability. Microwaves also enhanced cell disruption due to their high penetration capacity, thereby increasing mass transfer within and outside the plant tissues (Kumar, Smita, Kumar, Cumbal, & Rosero, 2014). Similar to ultrasound extraction, the use of microwave technology could reduce extraction time and energy consumed, less destructive effects and more yield. Despite the advantages, the high dependency of solvent and the extraction temperature limits the application of MAE.

As for a more complicated method, subcritical water extraction (SWE) is increasingly used in the preparation of environmental samples, and the extraction of natural products from herbs, plants, and foodstuffs (Lee et al., 2014; Munir, Kheirkhah, Baroutian, Quek, & Young, 2018; Kim, Ko, & Chung, 2019). Subcritical water, also called pressurized (hot) water refers to water at a temperature between 100 and 374 ^{o}C and pressure which is high enough to maintain the liquid state (below the critical pressure of 22 MPa) (Karakama, 2011). Ko, Cheigh, Cho, and Chung (2011) employed this technology to achieve quercetin yield over eight-, six-, and four-fold higher than those obtained by conventional extraction methods using ethanol, methanol, and water at the boiling point, respectively. These results indicated that SWE is a highly efficient method for recovering a valuable flavonoid and quercetin from onion skin and it is a potentially useful technique for the extraction of other flavonoids to be used in nutraceuticals. However, the high temperature may result in the degradation of flavonoids in onions.

Both advantages and disadvantages of several popular novel extraction methods have been reported pertinent to the extraction of flavonoid compounds from onions. Compared with traditional extraction methods, innovative extraction techniques generally require less extraction time, less energy consumed, better isolation, higher-quality extract, safer products, and lower environmental impact. On the other hand, these techniques can be expensive and constrained to certain conditions. For microwave-assisted extraction, little has been known about the optimal conditions for extracting bioactive compounds while ultrasound-assisted extraction needs to be undertaken carefully as it can degrade flavonoid compounds in a short period of time. Subcritical water extraction has a better extraction result in onions, however, it requires a strict temperature condition. The review shows that there is no such extraction technique alone as an ideal method. Since all the above novel extraction technologies have both advantages and disadvantages, selecting an ideal processing method needs to take into account the efficiency and reproducibility of extraction, the procedure, cost, time, safety, and automation degree. A combination of several technologies such as ultrasonic microwave-assisted extraction (UMAE) and microwave/ultrasonic-assisted enzymatic extraction (MUAEE) would be an option to obtain a better result in the future.

7. Conclusions

This paper reviewed different post-harvest storage factors that could potentially retain high-quality onion bulbs. These factors were mainly reviewed by storage conditions (temperature and time) and technologies (freeze-drying and packaging). The optimized storage conditions can be applied to reduce the loss of flavonoid content in both raw and processed onions. Some new techniques such as different drying methods (e.g. microwave and vacuum oven) that have been applied in onion production can help to retain onion quality and flavonoid compounds and increase its storage potential.

Food processing (thermal and non-thermal processing) operations, as the most effective and efficient way to reduce the loss of flavonoid compounds in onions, were further reviewed and discussed in this paper. It is suggested that onions should be cooked under a suitable time and temperature to inactivate the enzyme, for a reduction of the degradation of flavonoids. Moreover, several non-thermal processes such as high pressure or chemical solutions have been mostly investigated by previous studies as the enhanced extraction method of flavonoid compounds from onions.

The extraction of the flavonoids compounds in onions is of interest by many researchers, due to its potential health benefits. New extraction techniques, such as microwave-assisted extraction and ultrasound extraction have been widely used in the extraction of flavonoid compounds from onions. These novel methods are advantageous in comparison with conventional methods as the former requires a shorter extraction time and less organic solvents. Although novel extraction technologies showed a better potential to retain bioactive compounds, the use of novel methods needs further investigation towards industrial applications due to its high cost. Future research could focus on assessing the viability of the extraction methods economically.

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Table 1 Different classes of flavonoids and their substitution patterns.

Flavonols					
Position Compound	5	7	3’	4’	5’
Quercetin	OH	OH	OH	OH	-----
Kaempferol	OH	OH	-----	OH	-----
Myricetin	OH	OH	OH	OH	OH
Isorhamnetin	OH	OH	OCH_3	OH	-----
Flavones					
Position Compound	5	7	3’	4’	
Apigenin	OH	OH	-----	OH	
Luteolin	OH	OH	OH	OH	
Chrysin	OH	OH	-----	-----	

Flavan-3-ols						
Position Compound	3	5	7	3’	4’	5’
(+)-Catechin	βOH	OH	OH	OH	OH	-----
(–)-Epicatechin	αOH	OH	OH	OH	OH	-----
(–)-Epigallocatechin	αOH	OH	OH	OH	OH	OH
Flavanonol						
Position Compound	5	7	3’	4’		
Taxifolin	OH	OH	OH	OH		
Flavanones						
Position Compound	5	7	3’	4’		
Naringenin	OH	OH	-----	OH		
Hesperetin	OH	OH	OH	OCH_3		
Isoflavones						
Position Compound	5	7	4’			
Daidzein	-----	OH	OH			
Genistein	OH	OH	OH			
Anthocyanidins						
Position Compound	3	5	7	3’	4’	5’
Cyanidin	OH	OH	OH	OH	OH	-----
Cyanin	O-Glu	OH	OH	OH	OH	-----
Peonidin	OH	OH	OH	OCH_3	OH	-----
Delphinidin	-----	OH	OH	OH	-----	OH
Pelargonidin	OH	OH	OH	-----	OH	-----
Malvidin	OH	OH	OH	OCH_3	OH	OCH_3

(Source: Stalikas, 2007; Kumar & Pandey, 2013)

Table 2 Different minimal food processing and their effects on flavonoids content.

Minimal processing	Effects on flavonoids	References
Peeling	Reduction of 21% quercetins	Gennaro et al. (2002)
Chopping	No significant impact on quercetins content	Makris and Rossiter (2001); Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009)
Maceration (5 h)	Loss of quercetins between10.7% to 17.7%	Makris and Rossiter (2001)
Cutting	Induction of flavonol biosynthesis	Pérez-Gregorio et al. (2011a); Ioannou, Hafsa, Hamdi, Charbonnel, and Ghoul (2012); Bernaert, De Clercq, Van Bockstaele, De Loose, and Van Droogenbroeck (2013)
Trimming	Losses of 39% flavonoids	Ewald, Fjelkner-Modig, Johansson, Sjöholm, and Åkesson (1999)

Table 3 Influences of thermal processes on flavonoids content of onions.

Thermal processing	Impact on flavonoids	References
Mild-heat for 1 min at 60°C	20% increase	Siddiq, Roidoung, Sogi and Dolan (2013)
Griddled for 5mins at 110°C	57.35% increase	Juániz et al. (2016)
Boiling for 3 to 60 mins at 100°C	18% -75% decrease	Lombard, Peffley, Geoffriau, Thompson, and Herring (2005)
Boiling for 10 mins at 100°C	more than 20% decrease	Gorinstein et al. (2009)
Boiling for 60 mins at 100°C	more than 20% decrease	Makris and Rossiter (2001)
Blanching for 1.5 mins at 100°C	10-25% decrease	Gorinstein et al. (2009)
Baking for 15 mins	7-30% decrease	Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009)
Microwave cooking (450w) for 4 mins	no significant effects on quercetins	Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009)
Microwave cooking (750w) for 4 mins	16-20% decrease	Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009)
Microwave cooking (1200w) for 4 mins	no decrease on flavonoids	Ahmed and Eun (2017)
Frying for 5 or 15 mins at 180°C	23-39% decrease	Price, Bacon, and Rhodes (1997);Ewald et al. (1999); Lee et al. (2008)
Frying with oil for 4 or 8 mins at 180°C	no decrease on flavonoid	Ahmed and Eun (2017)
Oven roasting for 15 or 30 mins at 180°C	No modification of the total levels of quercetins	Rodrigues, Pérez-Gregorio, García-Falcón, and Simal-Gándara (2009)
Oven roasting for 18 mins at 270°C	15% decrease	Sans et al. (2019)
Sautéing for 5 mins	21% decrease	Lee et al. (2008)

Table 4 Previous studies on the use of novel techniques for extraction of onion flavonoid compounds.

Extraction techniques	plant material	Extraction flavonoids	Solvent	Comments	References
MAE	Edible of yellow onion	Flavonoids	No water or solvent	Easy to handle; green and economical rapid produce; less energy; working in the absence of any solvent or water in a short time resulting in a good percentage yield of flavonoids.	Zill-e-Huma et al. (2011); Kumar et al. (2014); Pal and Jadeja (2019)
PHWE-EEH	Edible of yellow onion	Querceitn glycosides	Water and ethanol	Higher quercetin extraction yield with a short period of time and reduced laboratory work and environmental impact; It is milder and more accurate.	Lindahl et al. (2013)
PHWE	Edible of onion and Onion by-products	Flavonoids	Water and ethanol	A quick, efficient and environmental friendly technique for extractions. Higher flavonoids extraction yield with a shorter extraction time.	Lindahl et al. (2010); Petersson et al. (2010); Liu et al. (2014)
PLE	The edible portion of onion	Quercetin	Methanol	Allow extraction of oxygen sensitive flavonoids; highly automated method but limited application in food industry due to the use of solvents.	Søltoft et al. (2009)
SFE	Skins of red and yellow onions	Quercetin aglycone	Ethanol	Controlled pressure and temperature conditions; rapid operation; low solvent consumption but high cost and long extraction time.	Martino and Guyer (2004); Campone et al., (2018)

SWE	Wastes of red and yellow onion skin	Quercetin Isorhamnetin	Water	More green procedure, but the temperature might cause degradation of compounds in onion.	Ko et al. (2011); Lee et al. (2014); Munir et al. (2018); Kim, Ko, and Chung, (2019)
UAE	Onion by-products	Flavonols	Water	Easy to use but high solvent consumption.	Jang et al. (2013); Katsampa et al. (2015)
PLPW	Onion by-products	Flavonoids	Water	An environmental friendly technology; providing high-quality and high-activity extracts without any solvent toxicity.	Manohar et al. (2017)
PEF	Onion bulb samples	Flavonoids	Water	A selective and environmental friendly process to recover water-soluble flavonoids from onion.	Liu, Zeng, and Ngadi, (2018)

Note: MAE - microwave assisted extraction, PHWE-EEH - pressurized hot water extraction-extraction-enzymatic hydrolysis, PHWE - pressurized hot water extraction, PLE - pressurized liquid extraction, SFE - supercritical fluid extraction, SWE - subcritical water extraction, UAE - ultrasound assisted extraction, PLPW - pressurized low polarity water, PEF - pulsed electric field.

Figure captions

Figure. 1 A. Basic structure of flavonoids.

Figure. 1 B. Chemical structure of the flavonoid.

Figure. 1 C. Structures of some main quercetins and its glucosides found in onion.

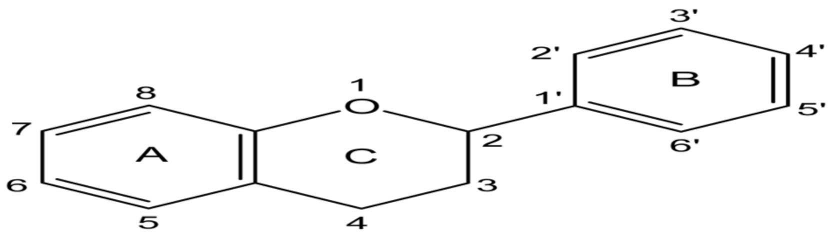

Fig 1 A – Basic structure of flavonoids (Wang, Li, & Bi, 2018).

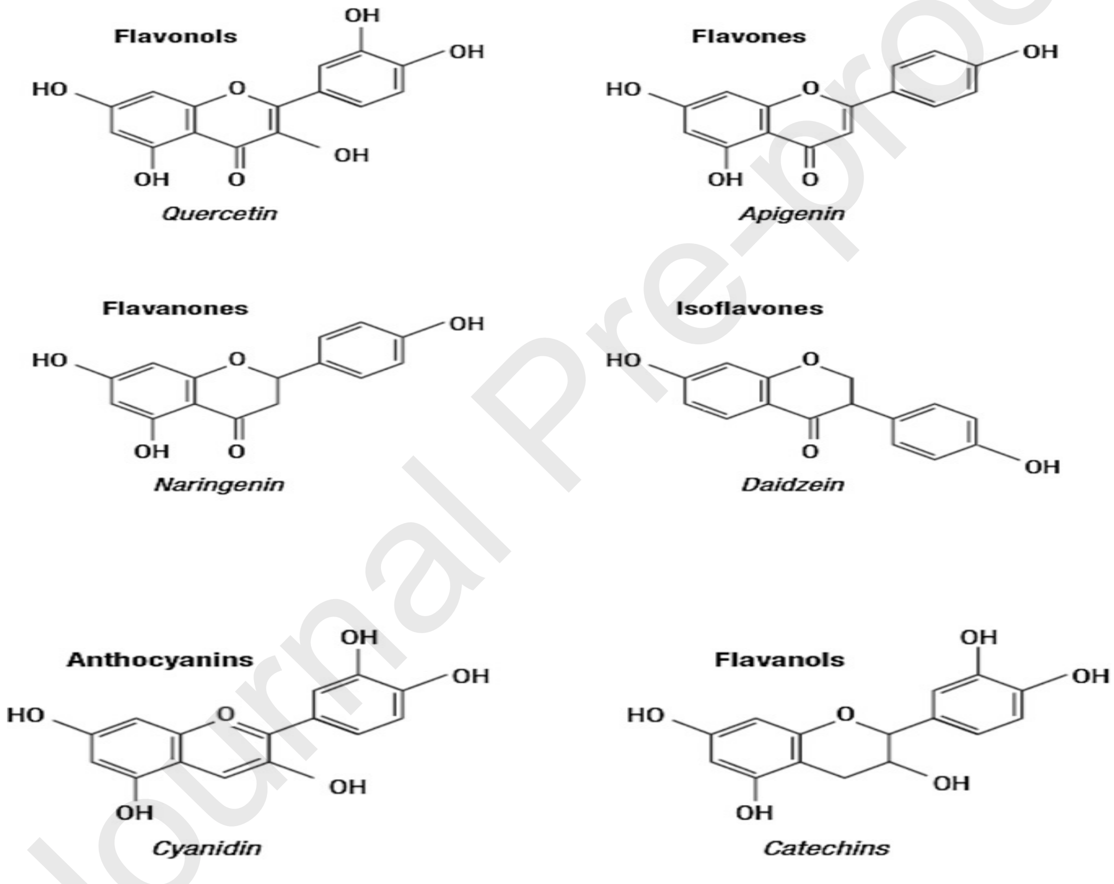

Fig 1 B – Chemical structure of the flavonoid (Ignat, Volf, & Popa, 2011).

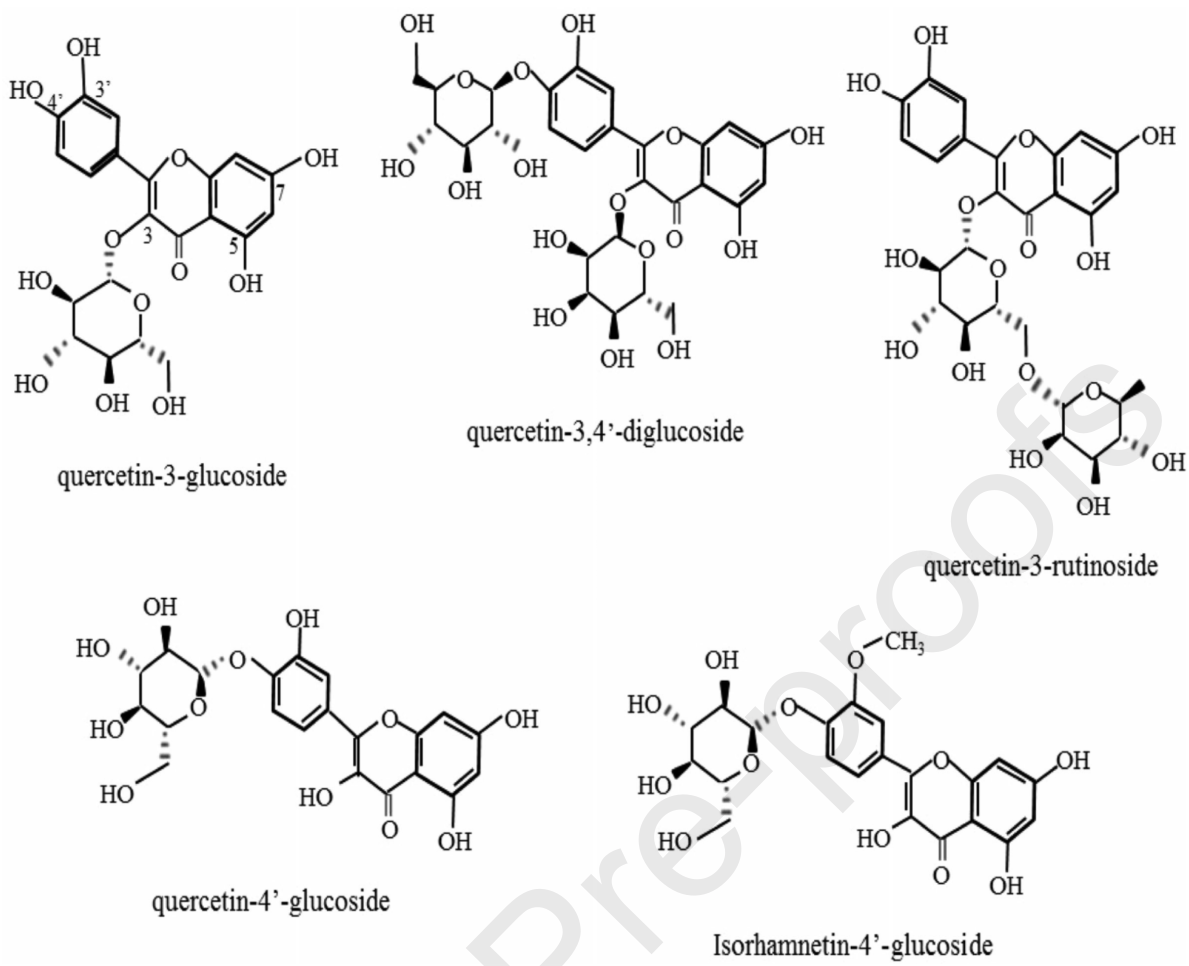

Fig 1 C – Structures of some main quercetins and its glucosides found in onion (Lee et al., 2008).

Dear Editor of Food Research International,

The authors report no conflict of interest.

Different factors influencing levels of flavonoids in onions

Post-harvest storage factors

- Storage conditions
- Storage technologies

Food processing factors

- Minimal processing
- Thermal processing
- Non-thermal processing

Different novel extraction methods

- Pressurized hot water extraction
- Ultrasound assisted extraction
- Microwave assisted extraction
- Subcritical water extraction

Highlights:

- The paper reviews post-harvest factors affecting onions' flavonoid compounds.
- Onion is one of the vegetables containing the highest content of flavonoids.
- Non-thermal processing treatment may have a profound effect on onion quality.
- Novel extraction techniques may contribute to flavonoid levels in onion.
- Flavonoids in onion by-products can be extracted as bioactive food ingredient.