Journal of Food Composition and Analysis 115 (2023) 105024

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Red-skinned onion phenolic compounds stability and bioaccessibility: A comparative study between deep-frying and air-frying

Alice Cattivelli, Adele Di Lorenzo, Angela Conte, Serena Martini, Davide Tagliazucchi *

Department of Life Sciences, University of Modena and Reggio Emilia, Via Amendola 2, 42100 Reggio Emilia, Italy

ARTICLE INFO

Keywords:
Mass spectrometry
Food processing
Bioaccessibility
Polyphenols
Gastro-intestinal digestion
Thermal treatments

ABSTRACT

In this study, the effect of deep-frying and air-frying on the stability and gastro-intestinal release of red-skinned onion phenolic compounds have been assessed by high-resolution mass spectrometry. Forty-four phenolic compounds were identified and quantified in raw onion. Both the frying treatments caused an increase in total phenolic compounds, which was more evident after air-frying (47.4% *vs* 18.6% increase). This increase was mainly a consequence of the water loss observed during frying. Quercetin was the most important phenolic compound detected both in raw and air-fried samples (99.5 ± 1.7 and 133 ± 2 μmol/100 g, respectively) while deep-fried onion was richer in quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside (48.7 ± 0.9 and 41.8 ± 0.3 μmol/100 g, respectively). After digestion, 38.6%, 60.5% and 89.6% of total phenolic compounds were bioaccessible in raw, deep-fried and air-fried onion. Air-fried onion exhibited the highest concentration of bioaccessible phenolic compounds (206 ± 1 μmol/100 g). Oxidative degradation and hydrolysis reactions of quercetin-hexosides occurred during *in vitro* digestion. Hence, air-frying can be considered a healthy cooking method able to preserve and release after digestion most of the health-promoting compounds found in raw onion and with a lower amount of fats and polar toxic compounds compared to deep-frying.

1. Introduction

Onion is an important component of the Mediterranean Diet and, more in general, is a vegetable food consumed widely worldwide either raw or after cooking. The intake of onion or an allium vegetables-enriched diet (garlic and onion) has been associated with a decreased risk of incidence of cardiovascular diseases, hypertension, gastro-intestinal tract cancers (such as oesophageal, gastric and colorectal cancers), type-2 diabetes and chronic kidney disease (Bahadoran et al., 2017; Wan et al., 2019). In the last years, numerous pieces of evidence have suggested that phenolic compounds present in onions might be responsible for the reported beneficial effects (Cattivelli et al., 2022; Kothari et al., 2020; Williamson, 2017). The main phenolic compounds identified in onion include flavonols, hydroxycinnamic acids and, in the red variety, anthocyanins (Cattivelli et al., 2021; Kothari et al., 2020). In particular, onion is rich in quercetin-derivatives, mainly quercetin aglycone, quercetin-mono-glucosides and quercetin-di-glucosides, which together may account for about 90% of onion phenolic compounds (Cattivelli et al., 2021; Kothari et al., 2020).

Food cooking has undoubtedly played a pivotal role in human evolution by promoting an increase in digestibility and consequent absorption of nutrients and producing healthier and more palatable foods (Pellegrini and Fogliano, 2017; Van Boekel et al., 2010). In the modern era, numerous cooking methods, such as boiling, steaming, frying, sautéing and microwaving, can be applied to food, depending on the culinary practices of the different countries. Cooking may trigger different modifications in the physical properties of foods from a chemical and biochemical point-of-view (Fabbri and Crosby, 2016; Van Boekel et al., 2010). Clearly, the distinctive employed processes may have a different effect on the physical modification and chemical/biochemical reactions. This is dependent on the different applied temperatures, the cooking time and the medium (Fabbri and Crosby, 2016; Van Boekel et al., 2010). In general, cooking has several beneficial effects encompassing food safety (inactivation of pathogens and toxins), nutrition (increased bioavailability of nutrients), sensorial aspects (flavour, texture and food appearance) as well as health benefits (release of phytochemicals and generation of new bioactive molecules such as melanoidins) (Palermo et al., 2014; Pérez-Burillo et al., 2019; Van Boekel et al., 2010). Contrariwise, some undesirable reactions may occur during food cooking leading to the production of potentially

* Corresponding author.
E-mail address: davide.tagliazucchi@unimore.it (D. Tagliazucchi).

https://doi.org/10.1016/j.jfca.2022.105024
Received 14 June 2022; Received in revised form 27 October 2022; Accepted 2 November 2022
Available online 3 November 2022

carcinogenic compounds and loss of nutrients (Koszucka and Nowak, 2019; Seal et al., 2008).

Among the different cooking techniques, deep-frying is one of the most frequently utilized both at the domestic and industrial levels. Its wide use lies in its capacity to confer exclusive sensorial properties to the food. Chemical changes in food induced by deep-frying may be either positive or negative for human health. Among the positive effects, several studies have pointed out that deep-frying increases the extractability and the bioaccessibility of phenolic compounds. For example, deep-frying increased the amount of extractable phenolic compounds as well as their bioaccessibility in onion, eggplant, cardoon, green pepper, and cactus cladodes in comparison with raw or foods cooked with different techniques (Cattivelli et al., 2021; De Santiago et al., 2018; Juániz et al., 2016a; Juániz et al., 2017; Martini et al., 2021a). As recently reported, the increased bioaccessibility of phenolic compounds after deep-frying positively modulates the biological activity of the food. Deep-fried and *in vitro* digested red-skinned onion and eggplant showed better anti-diabetic properties than raw, boiled, grilled and baked samples (Cattivelli et al., 2022). Similarly, cooking and *in vitro* digestion of cactus cladodes (including deep-frying) resulted in a higher anti-genotoxic effect on HT-29 cells compared to the raw sample (De Santiago et al., 2019). The negative aspects linked to deep-frying are related to the incorporation of fat that sometimes may reach an amount near 40% of the final food mass (Santos et al., 2017; Tian et al., 2016). Indeed, deep-frying led to the accumulation of some toxic products such as lipid oxidation products and acrylamide in the food (Santos et al., 2017). These compounds may be responsible for the progression of some chronic diseases such as cardiovascular diseases and cancer (Martini et al., 2021b; Zaghi et al., 2019). Moreover, individuals who eat fried foods are more prone to develop obesity and related diseases (Zaghi et al., 2019). For these motives, the consumers' tendency is directed towards the consumption of low-fat and healthier foods (Zaghi et al., 2019).

Recently, air-frying has been proposed as a healthier alternative technology to produce fried foods with similar sensorial and textural properties as deep-fried foods but with a lower amount of fats (Santos et al., 2017; Zaghi et al., 2019). Prior to concluding that air-frying is a healthy method due to the reduced quantity of incorporated oil, it is also necessary to consider the effect it may have on the stability and bioaccessibility of phenolic compounds. Until now, only one study carried out on purple-fleshed potatoes compared the effect of deep-frying and air-frying on the stability of phenolic compounds (Tian et al., 2016). They concluded that air-frying caused a greater loss of total phenolic compounds and chlorogenic acids compared to deep-frying (Tian et al., 2016). However, the stability of phenolic compounds not only depends on the cooking technique but also food matrix and phenolic compound structure (Cattivelli et al., 2021; De Santiago et al., 2018; Juániz et al., 2016a; Juániz et al., 2017; Martini et al., 2021a). Indeed, to the best of our knowledge, no studies have been carried out about the *in vitro* digestion fate and bioaccessibility of phenolic compounds in vegetable matrices following air-frying.

Therefore, the aim of this study was to compare the stability and bioaccessibility after *in vitro* digestion of red-skinned onion phenolic compounds in both raw, deep-fried and air-fried samples.

2. Materials and methods

2.1. Materials

The organic solvents (acetonitrile and methanol) as well as formic acid for high-resolution mass spectrometry and the extraction of phenolic compounds were supplied by BioRad (Hercules, CA, USA). Standards for phenolic compounds quantification as well as all other analytical reagents including enzymes for the *in vitro* digestion were obtained from Sigma-Aldrich (Milan, Italy) except for quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside that were obtained from Extrasynthese (Genay, France). The following standards were used for phenolic compound quantification: 4-hydroxybenzoic acid (purity ≥99%), protocatechuic acid (purity ≥99%), vanillic acid (purity ≥99%), sinapic acid (purity ≥98%), ferulic acid (purity ≥99%), quercetin (purity ≥95%), quercetin-3-*O*-glucoside (purity ≥98%), quercetin-4'-*O*-glucoside (purity ≥99%), quercetin-3-O-glucoside-4'-*O*-glucoside (purity ≥99%), kaempferol-3-*O*-glucoside (purity ≥98%), epicatechin (purity ≥98%) and cyanidin-3-*O*-glucoside (purity ≥98%). Red-skinned onion samples (*Allium cepa* L.) and sunflower oil (Italian Coop brand) were bought in a local supermarket (Reggio Emilia, Italy).

2.2. Frying treatments

After peeling, red-skinned onion samples were cut longitudinally into thin slices of about 0.5 cm. Each cooking treatment was carried out three times using a single onion for each set of experiments in order to have three biological replicates for each frying process.

The deep-frying procedure was performed in a domestic deep-fryer and red-skinned onion slices were fried at 140 °C for 10 min in sunflower oil. The onion-to-oil ratio was set at 1:10 (w/v). After frying, excess oil was absorbed by using a paper towel. The air-frying treatment was carried out in a commercial air-fryer. A portion of red-skinned onion slices was mixed with sunflower oil (onion-to-oil ratio of 1:0.03 w/v) and air-fried for 10 min at 200 °C. The cooking parameters are reported in Table 1. Water loss after cooking was determined gravimetrically. The cooking time and temperatures have been selected empirically based on preliminary tests in order to obtain well-cooked samples with the correct taste and texture, simulating domestic cooking conditions. The onion-to-oil ratios have been selected based on supplier indications.

The air fryer belongs to the Masterpro line by Carlo Cracco, a brand of Bergner Italy srl. Power: 1000 W, Capacity: 2 L. The deep fryer belongs to the Moulinex brand model AF2031, capacity 1 kg for 4 persons, oil capacity 1.8 L.

After cooking samples were stored at − 80 °C until the analysis.

2.3. In vitro digestion of raw, deep-fried and air-fried red-skinned onion

The *in vitro* digestion protocol INFOGEST 2.0, developed within the COST Action INFOGEST and further updated by Brodkorb et al. (2019) was applied to simulate gastro-intestinal digestion of raw and cooked red-skinned onion. The applied protocol mimicked the oral, gastric and intestinal phases of digestion. The complete procedure and the composition of the digestive juices are fully described in Brodkorb et al. (2019). Briefly, 1 g of raw or fried red-skinned onion was mixed with 1 mL of salivary fluid and homogenised with a laboratory blender (Waring® laboratory blender, Sigma-Aldrich, Milan, Italy) at 1000 rpm for 10 s. After the addition of 150 U/mL of salivary α-amylase (final concentration in the salivary fluid), the samples were incubated in a rotating wheel (10 rpm) at 37 °C for 2 min. Next, 5 mL of gastric fluid was added to the bolus, and the pH was corrected to 3 by using HCl 6 mol/L and 2000 U/mL of pepsin (final concentration in the gastric fluid) were further added to start the gastric phase of the digestion. The gastric step was carried out at 37 °C in a rotating wheel (10 rpm) for 120 min. At the end of this step, 4 mL of intestinal fluid was added to the gastric digested samples, the pH was raised to 7.5 and the samples were incubated for 30 min before adding pancreatin (200 U/mL based on trypsin activity; final concentration in the intestinal fluid)). Then, the intestinal step was carried out for 120 min at 37 °C in a rotating wheel (10 rpm). At the end of the digestion, the samples were centrifuged (10000 *g*, 20 min, 4 °C) and filtered through a 0.22 μm syringe filter before injection in the mass spectrometer.

All the digestions were carried out in triplicate for each prepared sample.

Table 1
Red-skinned onion cooking parameters and water loss during frying.

	Slice thickness (cm)	Cooking temperature (°C)	Cooking time (min)	Initial weight (g)	Final weight (g)	Weight loss (%)	Initial/final weight ratio
Deep-frying	0.5	140	10	200	80.2	59.9	2.49
Air-frying	0.5	200	10	200	84.2	57.9	2.38

2.4. Analysis of individual phenolic compounds stability after frying by high-resolution mass spectrometry (UHPLC/HR-MS)

Phenolic compounds were extracted from raw and fried red-skinned onion samples before digestion following the protocol reported by Martini et al. (2021a). Briefly, 15 g of red-skinned onion samples were mixed with 30 mL of the extraction solution composed of methanol/water/formic acid (70:28:2, v/v/v) and homogenized at 6000 rpm for 30 snds with an Ultra-Turrax (Heidolph DIAX900, Sigma-Aldrich, Milan, Italy). After 30 min of incubation at 37 °C, the mixtures were centrifuged (6000 *g*, 20 min, 4 °C) and the supernatants were filtered on paper (Whatman filter paper grade 1, Sigma-Aldrich, Milan, Italy).

High-resolution mass spectrometry was carried out by using a chromatographic separation module UHPLC Ultimate 3000 coupled with a Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Phenolic compounds separation was performed with a C18 column (Acquity UPLC HSS C18 Reversed phase, 2.1 × 100 mm, 1.8 μm particle size, Waters, Milan, Italy). The composition of the mobile phases, the elution gradient and the mass spectrometry parameters are fully described in Martini et al. (2020). Briefly, the mobile phase A was water/formic acid (99:1, v /v) whereas the mobile phase B was acetonitrile. The gradient began at 1% B and was then incremented to 40% B linearly in 20 min and then to 99% in 6 min. The flow rate was 0.3 mL/min. Quantification was carried out by building external calibration curves with the available standard compounds as depicted in Table S1.

Data are expressed as μmol/100 g of fresh raw or cooked onion.

2.5. Bioaccessibility determination of individual phenolic compounds after frying and in vitro digestion by high-resolution mass spectrometry

Samples collected at the end of the *in vitro* gastro-intestinal digestion were directly injected into UHPLC/HR-MS without any further handling. High-resolution mass spectrometry experiments were carried out as described above.

The bioaccessibility index was calculated as follows:

$$Bioaccessibility = \frac{Cd}{Ce} * 100$$

C*d* is the concentration of phenolic compounds after *in vitro* digestion whereas C*e* is the concentration before the *in vitro* digestion.

2.6. Statistics

Data are shown as mean ± SD for three replicates for each prepared sample. Graph Pad Prism 6.0 (GraphPad Software, San Diego, CA, U.S.A.) was used for the statistical analysis by applying univariate analysis of variance (ANOVA) with Tukey's post-hoc test. The differences were considered significant with $P < 0.05$.

3. Result and discussion

3.1. Phenolic profile of raw red skinned-onion

A total of 44 individual phenolic compounds were identified and quantified in raw onion samples, the class of flavonols being the most representative one (Table 2). Total flavonols content accounted for 87.8% of the total amount of phenolic compounds, followed by anthocyanins and hydroxycinnamic acids, which represented 6.1% and 6.0% of total phenolic compounds. Moreover, trace amounts of hydroxybenzoic acids, flavan-3-ols and dihydroflavonols were also detected (Table 2). Considering the individual phenolic compounds, the quantitative phenolic profile of raw red-skinned onion was dominated by quercetin, quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside, which together represented 82.0% of total phenolic compounds. Among the three flavonols, quercetin was the compound detected in the highest amount in the raw sample (63.8% of total phenolic compounds) followed by quercetin-4'-*O*-glucoside (10.2% of total phenolic compounds) and quercetin-3-*O*-glucoside-4'-*O*-glucoside (8.0% of total phenolic compounds). Additional compounds detected in an appreciable amount in the red-skinned onion raw sample were sinapic acid-hexoside isomer 2 (5.3% of total phenolic compounds), belonging to the hydroxycinnamic acid class, the anthocyanin cyanidin-*O*-malonyl-hexoside (4.3% of total phenolic compounds) and two further flavonols named isorhamnetin and isorhamnetin-4'-*O*-hexoside (representing the 2.0% and 2.5% of total phenolic compounds, respectively). These results are quite different compared to the previously reported data that reported a different quantitative phenolic profile in red-skinned onions (Cattivelli et al., 2021; Price et al., 1997; Rodrigues et al., 2009). However, the phenolic profile reported in this study strongly resembled that of the red onion variety Tropea rossa tonda which displayed high amounts of free quercetin and more quercetin-mono-hexosides compared to quercetin-di-glucosides (Marotti and Piccaglia, 2002). It is important to note that differences in the onion phenolic profile may be related to the onion variety, storage and climate conditions as well as the extraction procedure and instrumental analysis (Cattivelli et al., 2021; Patil et al., 1995; Price et al., 1997; Rodrigues et al., 2009).

In the present work, we used commercially available onions, bought at the food store, and no information is available on the onion variety, storage and other agro-climatic conditions, making it difficult to compare data. However, this study focused on the comparison of deep-frying and air-frying methods on the stability and bioaccessibility of red-skinned onion and not on gaining insight into the phenolic profile of a particular onion variety.

3.2. Effect of deep-frying and air-frying on red-skinned onion phenolic compounds stability

As reported in Table 2, both deep-frying and air-frying had a significant impact on the red-skinned onion qualitative and quantitative phenolic profile, although with substantial differences.

Considering the total concentration of phenolic compounds detected by mass spectrometry and referred to raw or cooked onion, both treatments caused an increase in extractable phenolic compounds, which was more evident after air-frying (+47.4%) than after deep-frying (+18.6%). Considering the single phenolic classes, the observed increase in phenolic compounds concentration was almost entirely due to an increase in the flavonol content (Table 2). In the deep-fried samples, the incidence of flavonols on total phenolic compounds was similar to that of the raw samples (89.2% in the deep-fried sample *vs* 87.8% in the raw one) whereas it increased to 96.5% in the air-fried sample. Considering the other phenolic classes, a substantial decrease of total hydroxycinnamic acids was recorded after both treatments, whereas the anthocyanin content only decreased after air-frying. In the deep-fried red-skinned onion samples, the total anthocyanin amount was increased by 81.1% compared to the raw sample and accounted for 9.4% of total phenolic compounds (Table 2). In accordance, previous studies found

Table 2
Concentration of individual phenolic compounds in raw and cooked red-skinned onion. Results are expressed in μmol of phenolic compound/100 g of raw or cooked onion. Values are expressed as average ± standard deviation (n = 3).

Compound	Raw red-skinned onion	Deep-fried red-skinned onion	Air-fried red-skinned onion
Hydroxybenzoic acids			
Hydroxybenzoic acid isomer 1	0.102 ± 0.013^{a}	0.139 ± 0.009^{b}	0.055 ± 0.007^{c}
Hydroxybenzoic acid isomer 2	n.d.	n.d.	0.048 ± 0.014
Protocatechuic acid	0.019 ± 0.001^{a}	0.144 ± 0.013^{b}	0.117 ± 0.015^{b}
Di-hydroxybenzoic acid isomer 1	0.024 ± 0.003^{a}	0.116 ± 0.012^{b}	0.038 ± 0.004^{a}
Di-hydroxybenzoic acid isomer 2	n.d.	n.d.	n.d.
Vanillic acid	0.015 ± 0.003^{a}	0.008 ± 0.004^{a}	0.037 ± 0.004^{b}
Di-hydroxybenzoic acid-*O*-hexoside isomer 1	0.048 ± 0.002^{a}	0.077 ± 0.001^{a}	0.066 ± 0.002^{a}
Di-hydroxybenzoic acid-*O*-hexoside isomer 2	0.019 ± 0.004^{a}	0.084 ± 0.005^{b}	0.085 ± 0.001^{b}
Di-hydroxybenzoic acid-*O*-hexoside isomer 3	0.025 ± 0.000^{a}	0.037 ± 0.001^{a}	0.044 ± 0.000^{a}
Total hydroxybenzoic acids	**0.252 ± 0.0144^{a}**	**0.605 ± 0.021^{b}**	**0.490 ± 0.002^{c}**
Hydroxycinnamic acids			
Sinapic acid	n.d.	0.088 ± 0.001^{a}	0.104 ± 0.013^{a}
Ferulic acid-4-*O*-hexoside	0.309 ± 0.032^{a}	0.723 ± 0.014^{b}	0.438 ± 0.011^{c}
Sinapic acid-*O*-hexoside isomer 1	0.835 ± 0.020^{a}	n.d.	1.12 ± 0.06^{b}
Sinapic acid-*O*-hexoside isomer 2	8.23 ± 0.18^{a}	0.659 ± 0.013^{b}	0.814 ± 0.010^{c}
Sinapic acid-*O*-hexoside isomer 3	n.d.	n.d.	0.443 ± 0.009
Total hydroxycinnamic acids	**9.37 ± 0.18^{a}**	**1.47 ± 0.02^{b}**	**2.92 ± 0.06^{c}**
Flavonols			
Quercetin	99.5 ± 1.7^{a}	48.8 ± 3.1^{b}	133 ± 2^{c}
Isorhamnetin	3.06 ± 0.19^{a}	1.24 ± 0.01^{b}	11.7 ± 0.2^{c}
Kaempferol-3-*O*-hexoside isomer 1	0.273 ± 0.010^{a}	1.62 ± 0.05^{b}	0.534 ± 0.032^{c}
Kaempferol-3-*O*-hexoside isomer 2	0.049 ± 0.014^{a}	0.035 ± 0.004^{a}	0.022 ± 0.005^{a}
Kaempferol-3-*O*-hexoside isomer 3	0.129 ± 0.010^{a}	0.043 ± 0.001^{b}	0.047 ± 0.000^{b}
Quercetin-3-*O*-hexoside	0.525 ± 0.079^{a}	2.69 ± 0.07^{b}	2.11 ± 0.04^{c}
Quercetin-4'-*O*-glucoside	15.9 ± 0.7^{a}	48.7 ± 0.9^{b}	34.2 ± 0.2^{c}
Isorhamnetin-3-*O*-hexoside	n.d.	0.415 ± 0.010^{a}	0.158 ± 0.013^{b}
Isorhamnetin-4'-*O*-hexoside	3.97 ± 0.08^{a}	13.0 ± 0.2^{b}	8.94 ± 0.61^{c}
Quercetin-7-*O*-acetylhexoside	0.035 ± 0.003^{a}	0.054 ± 0.001^{a}	0.029 ± 0.000^{a}
Isorhamnetin-*O*-hexoside-*O*-pentoside	0.054 ± 0.010^{a}	0.031 ± 0.003^{a}	0.018 ± 0.004^{a}
Kaempferol-*O*-hexoside-*O*-hexoside isomer 1	0.155 ± 0.002^{a}	0.209 ± 0.009^{b}	0.059 ± 0.000^{c}
Kaempferol-*O*-hexoside-*O*-hexoside isomer 2	0.115 ± 0.007^{a}	0.054 ± 0.003^{b}	0.037 ± 0.002^{b}
Quercetin-7-*O*-hexoside-4'-*O*-hexoside	0.088 ± 0.012^{a}	0.135 ± 0.001^{b}	0.102 ± 0.002^{a}
Quercetin-3-*O*-glucoside-4'-*O*-glucoside	12.5 ± 0.9^{a}	41.8 ± 0.3^{b}	29.8 ± 0.9^{c}
Isorhamnetin-3-*O*-hexoside-4'-*O*-hexoside	0.564 ± 0.041^{a}	2.50 ± 0.04^{b}	1.55 ± 0.07^{c}
Quercetin-*O*-hexoside-*O*-malonylhexoside isomer 1	0.025 ± 0.000^{a}	0.029 ± 0.000^{a}	0.015 ± 0.001^{a}
Quercetin-*O*-hexoside-*O*-malonylhexoside isomer 2	0.017 ± 0.004^{a}	0.044 ± 0.001^{a}	0.013 ± 0.002^{a}
Quercetin-tri-*O*-hexoside isomer 1	0.035 ± 0.001^{a}	0.067 ± 0.001^{b}	0.037 ± 0.001^{a}
Quercetin-tri-*O*-hexoside isomer 2	n.d.	3.50 ± 0.10^{a}	0.184 ± 0.007^{b}
Hydroxybenzoic acids			
Total flavonols	**137 ± 2^{a}**	**165 ± 3^{b}**	**222 ± 2^{c}**
Flavan-3-ols			
(Epi)catechin-*O*-hexoside isomer 1	0.024 ± 0.000^{a}	0.025 ± 0.001^{a}	0.009 ± 0.001^{a}
(Epi)catechin-*O*-hexoside isomer 2	0.015 ± 0.000^{a}	0.013 ± 0.004^{a}	n.d.
(Epi)catechin-*O*-hexoside isomer 3	0.012 ± 0.000^{a}	0.011 ± 0.002^{a}	n.d.
Total flavan-3-ols	**0.051 ± 0.00^{a}**	**0.049 ± 0.004^{a}**	**0.009 ± 0.001^{a}**
Dihydroflavonols			
Taxifolin-*O*-hexoside isomer 1	0.052 ± 0.007^{a}	0.193 ± 0.007^{b}	0.143 ± 0.011^{c}
Taxifolin-*O*-hexoside isomer 2	0.039 ± 0.002^{a}	0.103 ± 0.010^{b}	0.102 ± 0.004^{b}
Taxifolin-*O*-hexoside isomer 3	0.018 ± 0.000^{a}	0.225 ± 0.001^{b}	0.057 ± 0.002^{c}
Taxifolin-*O*-hexoside isomer 4	0.036 ± 0.003^{a}	0.094 ± 0.010^{b}	0.058 ± 0.011^{a}
Taxifolin-*O*-hexoside isomer 5	0.035 ± 0.002^{a}	0.053 ± 0.000^{a}	0.044 ± 0.001^{a}
Total dihydroflavonols	**0.180 ± 0.008^{a}**	**0.668 ± 0.016^{b}**	**0.404 ± 0.016^{c}**
Anthocyanins			
Cyanidin-3-*O*-hexoside isomer 1	0.884 ± 0.062^{a}	2.84 ± 0.07^{b}	0.703 ± 0.040^{c}
Cyanidin-3-*O*-hexoside isomer 2	0.115 ± 0.011^{a}	0.034 ± 0.003^{b}	0.044 ± 0.001^{b}
Peonidin-3-*O*-hexoside	0.115 ± 0.002^{a}	0.751 ± 0.043^{b}	0.105 ± 0.009^{a}
Cyanidin-*O*-malonyl-hexoside	6.69 ± 0.24^{a}	10.67 ± 0.11^{b}	2.92 ± 0.04^{c}
Peonidin-*O*-malonyl-hexoside	0.108 ± 0.010^{a}	0.193 ± 0.070^{a}	0.008 ± 0.007^{a}
Cyanidin-*O*-hexoside-*O*-hexoside isomer 1	n.d.	0.084 ± 0.001^{a}	0.022 ± 0.000^{b}
Cyanidin-*O*-hexoside-*O*-hexoside isomer 2	0.423 ± 0.014^{a}	0.673 ± 0.031^{b}	0.175 ± 0.002^{c}
Cyanidin-*O*-hexoside-*O*-hexoside isomer 3	0.094 ± 0.010^{a}	0.034 ± 0.001^{b}	0.035 ± 0.004^{b}
Cyanidin-*O*-hexoside-*O*-malonylhexoside	1.13 ± 0.08^{a}	2.02 ± 0.06^{b}	0.415 ± 0.013^{c}
Total anthocyanins	**9.56 ± 0.26^{a}**	**17.3 ± 0.2^{b}**	**4.43 ± 0.06^{c}**
Total	**156 ± 2^{a}**	**185 ± 3^{b}**	**230 ± 2^{c}**

Different letters within the same row mean significant different ($P < 0.05$) values.
n.d. means that the compound was not detected in the sample

that deep-frying increased the flavonol content in yellow and red-skinned onions (Cattivelli et al., 2021; Harris et al., 2015; Juániz et al., 2016a; Lombard et al., 2005; Makris and Rossiter, 2001). However, other researchers found that the flavonoid content decreased after deep-frying in green pepper and cactus cladodes (De Santiago et al., 2018; Juániz et al., 2016b).

Among the individual phenolic compounds, a significant increase of both quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside was ascertained in deep-fried and air-fried samples, in comparison with the raw one. The highest increase for both the quercetin-derivatives was observed for the deep-fried onion samples (Table 2). Conversely, quercetin aglycone showed a different behaviour depending on the treatment. In the air-fried samples, the amount of quercetin aglycone increased by 33.5% compared to the raw samples, whereas it decreased by 50.9% in deep-fried onions. Differently from raw and air-fried samples, where quercetin aglycone was the most representative compound, in the deep-fried samples the flavonol that was present in the highest amount was quercetin-4'-*O*-glucoside. Concerning the isorhamnetin-derivatives, in the air-fried samples, a substantial increase in isorhamnetin aglycone and isorhamnetin-4'-*O*-hexoside was recorded

compared to the raw samples, while in the deep-fried samples only isorhamnetin-4'-*O*-hexoside increased after the treatment. According to the behaviour of quercetin aglycone, also the amount of isorhamnetin aglycone was lower in the deep-fried samples compared to the raw samples (Table 2). Finally, some new compounds, although in low concentrations, appeared after deep-frying and air-frying. The increase in phenolic compound concentration described after deep-frying and air-frying could be due to the matrix softening effect caused by high temperature, which made phenolic compounds more easily extractable, or to the loss of water recorded during cooking (Cattivelli et al., 2021; Palermo et al., 2014; Zhao et al., 2019).

To better understand the effect of the two frying treatments on the phenolic compound stability, the data reported in Table 2 were corrected for the weight loss (see Table 1 for the initial to final weight ratio) monitored during the frying procedures. As depicted in Fig. 1A-C, both treatments provoked a significant decrease in the amount of total

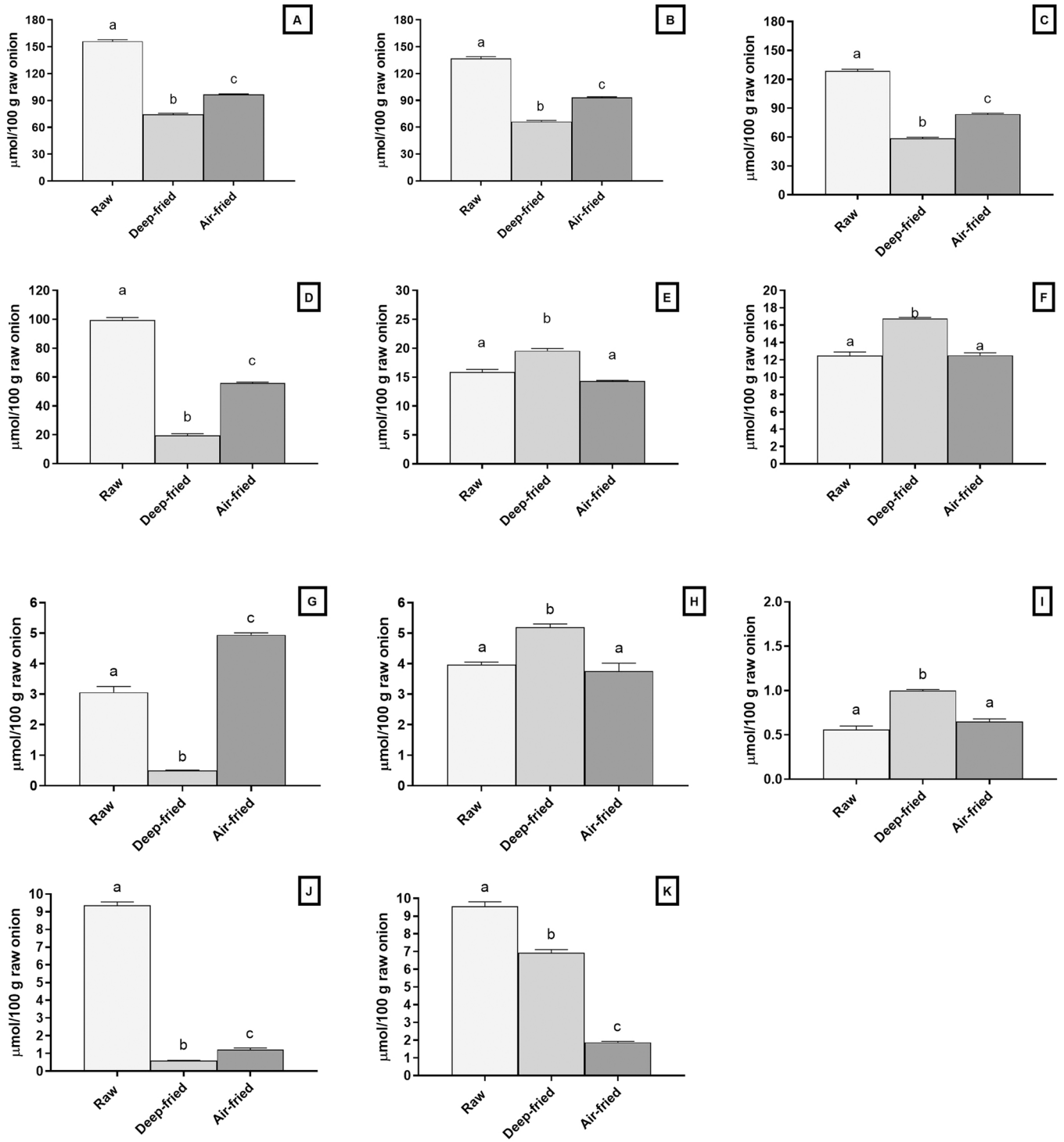

Fig. 1. Effect of deep-frying and air-frying on red-skinned onion phenolic compounds referred to the original fresh weight. (A) Total phenolic compounds. (B) Total flavonols. (C) Total quercetin-derivatives. (D) Quercetin. (E) Quercetin-4'-*O*-hexoside. (F) Quercetin-3-*O*-hexoside-4'-*O*-hexoside. (G) Isorhamnetin. (H) Isorhamnetin-4'-*O*-hexoside. (I) Isorhamnetin-3-*O*-hexoside-4'-*O*-hexoside. (J) Total hydroxycinnamic acids. (K) Total anthocyanins. Results are expressed as µmol/100 g of fresh weight. Different letters mean significant difference ($P < 0.05$).

phenolic compounds, total flavonols and total quercetin-derivatives, which was more pronounced after deep-frying. In this last sample, reductions of 52.4%, 50.0% and 54.5% were noted for total phenolic compounds, total flavonols and total quercetin-derivatives, respectively. Whereas, after air-frying, the loss was more limited with a recorded decrease of 38.1%, 31.9% and 34.8% for total phenolic compounds, total flavonols and total quercetin-derivatives, respectively. Looking at the behaviour of the three most important phenolic compounds (Fig. 1D-

Table 3
Concentration of individual phenolic compounds in raw and cooked red-skinned onion. Results are expressed in μmol of phenolic compound/100 g of raw or cooked onion. Values are expressed as average ± standard deviation (n = 3). Bioaccessibility index (BI) is defined as the ratio between the amount of a specific phenolic compound after *in vitro* digestion and the amount in the solvent extract expressed as percentage value.

Compound	Raw red-skinned onion	BI (%)	Deep-fried red-skinned onion	BI (%)	Air-fried red-skinned onion	BI (%)
Hydroxybenzoic acids						
Hydroxybenzoic acid isomer 1	0.051 ± 0.001^{a}	50.0	0.044 ± 0.003^{a}	28.6	0.029 ± 0.004^{a}	60.0
Hydroxybenzoic acid isomer 2	0.073 ± 0.000^{a}	n.f.	0.048 ± 0.000^{a}	n.f.	0.065 ± 0.004^{a}	120
Protocatechuic acid	0.218 ± 0.000^{a}	1100	0.054 ± 0.001^{b}	35.7	0.078 ± 0.002^{c}	66.7
Di-hydroxybenzoic acid isomer 1	1.14 ± 0.02^{a}	5700	0.043 ± 0.000^{b}	33.3	0.049 ± 0.001^{b}	125
Di-hydroxybenzoic acid isomer 2	0.472 ± 0.021^{a}	n.f.	0.414 ± 0.001^{b}	n.f.	0.513 ± 0.014^{c}	n.f.
Vanillic acid	0.041 ± 0.000^{a}	400	0.022 ± 0.00^{a}	200	0.025 ± 0.001^{a}	50.0
Di-hydroxybenzoic acid-*O*-hexoside isomer 1	n.d.	0.000	n.d.	0.000	n.d.	0.000
Di-hydroxybenzoic acid-*O*-hexoside isomer 2	2.79 ± 0.20^{a}	13950	0.613 ± 0.019^{b}	762	0.991 ± 0.020^{c}	1237
Di-hydroxybenzoic acid-*O*-hexoside isomer 3	n.d.	0.000	n.d.	0.000	n.d.	0.000
Total hydroxybenzoic acids	**4.78 ± 0.20^{a}**	**1992**	**1.24 ± 0.02^{b}**	**200**	**1.75 ± 0.02^{c}**	**355**
Hydroxycinnamic acids						
Sinapic acid	0.079 ± 0.000^{a}	n.f.	0.022 ± 0.001^{b}	22.2	0.095 ± 0.000^{a}	90.0
Ferulic acid-4-*O*-hexoside	0.104 ± 0.004^{a}	32.3	0.358 ± 0.021^{b}	50.0	0.594 ± 0.010^{c}	134
Sinapic acid-*O*-hexoside isomer 1	1.02 ± 0.02^{a}	123	0.277 ± 0.020^{b}	n.f.	1.40 ± 0.07^{c}	125
Sinapic acid-*O*-hexoside isomer 2	0.304 ± 0.024^{a}	3.60	0.095 ± 0.000^{b}	13.6	0.607 ± 0.021^{c}	74.1
Sinapic acid-*O*-hexoside isomer 3	n.d.	0.000	n.d.	0.000	0.439 ± 0.012	100
Total hydroxycinnamic acids	**1.51 ± 0.03^{a}**	**16.0**	**0.75 ± 0.03^{b}**	**51.0**	**3.13 ± 0.07^{c}**	**107.2**
Flavonols						
Quercetin	24.2 ± 0.1^{a}	24.3	88.7 ± 3.4^{b}	182	134 ± 1^{c}	101
Isorhamnetin	n.d.	0.000	5.42 ± 0.27^{a}	437	3.62 ± 0.19^{b}	30.8
Kaempferol-3-*O*-hexoside isomer 1	n.d.	0.000	0.012 ± 0.001^{a}	0.604	0.019 ± 0.000^{a}	1.90
Kaempferol-3-*O*-hexoside isomer 2	n.d.	0.000	0.010 ± 0.000^{a}	33.3	0.019 ± 0.003^{a}	50.0
Kaempferol-3-*O*-hexoside isomer 3	0.102 ± 0.010^{a}	76.9	0.018 ± 0.000^{b}	25.0	0.024 ± 0.001^{b}	40.0
Quercetin-3-*O*-hexoside	0.133 ± 0.010^{a}	25.0	0.964 ± 0.032^{b}	35.7	3.830 ± 0.033^{c}	181
Quercetin-4'-*O*-glucoside	13.9 ± 0.4^{a}	87.4	5.58 ± 0.82^{b}	11.5	24.6 ± 0.1^{c}	71.9
Isorhamnetin-3-*O*-hexoside	0.039 ± 0.000^{a}	n.f.	0.115 ± 0.000^{b}	26.8	0.078 ± 0.010^{c}	50.0
Isorhamnetin-4'-*O*-hexoside	6.20 ± 0.53^{a}	156	1.79 ± 0.05^{b}	13.9	6.76 ± 0.41^{a}	75.6
Quercetin-7-*O*-acetylhexoside	0.021 ± 0.000^{a}	66.7	0.014 ± 0.001^{a}	20.0	0.009 ± 0.002^{a}	33.3
Isorhamnetin-*O*-hexoside-*O*-pentoside	0.015 ± 0.010^{a}	20.0	0.021 ± 0.000^{a}	66.7	0.024 ± 0.001^{a}	100
Kaempferol-*O*-hexoside-*O*-hexoside isomer 1	n.d.	0.000	n.d.	0.000	n.d.	0.000
Kaempferol-*O*-hexoside-*O*-hexoside isomer 2	0.034 ± 0.002^{a}	27.3	0.014 ± 0.001^{a}	20.0	0.023 ± 0.002^{a}	50.0
Quercetin-7-*O*-hexoside-4'-*O*-hexoside	0.069 ± 0.010^{a}	77.8	0.054 ± 0.001^{a}	38.5	0.043 ± 0.000^{a}	40.0
Quercetin-3-*O*-glucoside-4'-*O*-glucoside	8.55 ± 0.53^{a}	68.4	6.79 ± 0.65^{b}	16.2	27.5 ± 0.2^{c}	92.3
Isorhamnetin-3-*O*-hexoside-4'-*O*-hexoside	0.341 ± 0.010^{a}	60.7	0.447 ± 0.010^{b}	18.0	0.395 ± 0.014^{a}	25.2
Quercetin-*O*-hexoside-*O*-malonylhexoside isomer 1	0.015 ± 0.010^{a}	50.0	0.012 ± 0.000^{a}	33.3	0.014 ± 0.001^{a}	100
Quercetin-*O*-hexoside-*O*-malonylhexoside isomer 2	n.d.	0.000	n.d.	0.000	n.d.	0.000
Quercetin-tri-*O*-hexoside isomer 1	n.d.	0.000	n.d.	0.000	n.d.	0.000
Quercetin-tri-*O*-hexoside isomer 2	n.d.	0.000	n.d.	0.000	n.d.	0.000
Total flavonols	**53.6 ± 0.8^{a}**	**39.1**	**110 ± 4^{b}**	**66.7**	**201 ± 1^{c}**	**90.5**
Flavan-3-ols						
(Epi)catechin-*O*-hexoside isomer 1	n.d.	0.000	n.d.	0.000	n.d.	0.000
(Epi)catechin-*O*-hexoside isomer 2	n.d.	0.000	n.d.	0.000	n.d.	0.000
(Epi)catechin-*O*-hexoside isomer 3	n.d.	0.000	n.d.	0.000	n.d.	0.000
Total flavan-3-ols	**n.d.**	**0.000**	**n.d.**	**0.000**	**n.d.**	**0.000**
Dihydroflavonols						
Taxifolin-*O*-hexoside isomer 1	n.d.	0.000	0.034 ± 0.000^{a}	15.8	0.058 ± 0.001^{b}	42.9
Taxifolin-*O*-hexoside isomer 2	n.d.	0.000	n.d.	0.000	0.035 ± 0.000	30.0
Taxifolin-*O*-hexoside isomer 3	n.d.	0.000	n.d.	0.000	n.d.	0.000
Taxifolin-*O*-hexoside isomer 4	0.013 ± 0.000^{a}	25.0	0.025 ± 0.020^{a}	22.2	0.018 ± 0.002^{a}	33.3
Taxifolin-*O*-hexoside isomer 5	n.d.	0.000	0.015 ± 0.000^{a}	20.0	0.015 ± 0.000^{a}	25.0
Total dihydroflavonols	**0.013 ± 0.000^{a}**	**5.6**	**0.074 ± 0.02^{b}**	**9.2**	**0.126 ± 0.002^{c}**	**30.0**
Anthocyanins						
Cyanidin-3-*O*-hexoside isomer 1	0.009 ± 0.020^{a}	1.10	0.025 ± 0.000^{a}	0.75	0.044 ± 0.001^{b}	5.73
Cyanidin-3-*O*-hexoside isomer 2	0.100 ± 0.011^{a}	90.9	0.014 ± 0.001^{b}	33.3	0.015 ± 0.000^{b}	25.0
Peonidin-3-*O*-hexoside	0.014 ± 0.000^{a}	9.12	0.010 ± 0.000^{a}	1.31	0.010 ± 0.000^{a}	10.0
Cyanidin-*O*-malonylhexoside	0.079 ± 0.010^{a}	1.25	0.214 ± 0.010^{b}	2.00	0.275 ± 0.013^{b}	9.22
Peonidin-*O*-malonylhexoside	0.011 ± 0.004^{a}	9.10	0.015 ± 0.003^{a}	5.33	0.015 ± 0.004^{a}	11.1
Cyanidin-*O*-hexoside-*O*-hexoside isomer 1	n.d.	0.0	n.d.	0.0	n.d.	0.0
Cyanidin-*O*-hexoside-*O*-hexoside isomer 2	0.024 ± 0.000^{a}	4.84	0.011 ± 0.000^{a}	1.53	0.013 ± 0.000^{a}	5.95
Cyanidin-*O*-hexoside-*O*-hexoside isomer 3	0.025 ± 0.001^{a}	22.2	0.012 ± 0.000^{a}	33.3	0.025 ± 0.003^{a}	66.7
Cyanidin-*O*-hexoside-*O*-malonylhexoside	0.024 ± 0.001^{a}	1.82	0.039 ± 0.001^{a}	2.04	0.056 ± 0.000^{a}	12.2
Total anthocyanins	**0.286 ± 0.02^{a}**	**2.8**	**0.340 ± 0.001^{b}**	**1.9**	**0.453 ± 0.003^{c}**	**9.4**
Total	**60.2 ± 0.8^{a}**	**38.6**	**112 ± 4^{b}**	**60.5**	**206 ± 1^{c}**	**89.6**

Different letters within the same row mean significant different ($P < 0.05$) values.
n.d. means that the compound was not detected in the sample
n.f. means newly formed compound

F), it is clear that quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside were more stable compared to the quercetin aglycone. High recoveries of quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside were observed after air-frying (90.4% and 100% of recovery) whereas in the deep-fried samples the amount of these two compounds was significantly higher than in the raw sample. This effect may be a consequence of the release of quercetin-4'-*O*-glucoside and quercetin-3-*O*-glucoside-4'-*O*-glucoside strongly linked to onion macromolecules, such as proteins or polysaccharides, favoured by the matrix softening effect due to the thermal treatment (Harris et al., 2015; Juániz et al., 2016a; Lombard et al., 2005). Alternatively, the reported increase may result from the thermal degradation of more complex quercetin derivatives not identified in the present study (Cattivelli et al., 2021; Juániz et al., 2016a). The same behaviour can be seen for glycosylated isorhamnetin derivatives as shown in Fig. 1G-I.

Diversely from the glycosylated flavonols, the corresponding aglycones had a different trend depending on the frying procedure (Fig. 1D and G). The quercetin content decreased both in the deep-fried and air-fried onion samples but to a different extent. In the air-fried samples, the recorded decrease was 43.9% whereas a strong reduction of 80.3% in the quercetin content was observed after deep-frying. This decrease in quercetin concentration after frying could originate from leaching by the cooking oil (Ambra et al., 2022). Rinaldi de Alvarenga et al. (2019) found that after frying, extra-virgin olive oil was enriched in quercetin and other phenolic compounds (such as naringenin) deriving from onion and tomato used for the preparation of the sofrito. Similarly, Ramírez-Anaya et al. (2019) identified several phenolic compounds in extra-virgin olive oil that were incorporated into the oil after deep-frying eggplant and tomato. The highest decrease in quercetin content observed after deep-frying in this study may be due to the greater amount of oil used in the deep-frying experiments compared to the air-frying experiments. Although thermal degradation of quercetin can not be excluded, no previously reported degradation products of quercetin were identified in the mass spectra (Fuentes et al., 2017; Rohn et al., 2007). Similar behaviour was also observed for isorhamnetin after deep-frying (83.7% decrease compared to the raw sample); however, in the air-fried samples, an increase of 61.4% of isorhamnetin concentration was ascertained compared to the raw sample.

With respect to the minor phenolic compounds, a great decrease of 93.7% and 87.0% in hydroxycinnamic acid concentration was observed after deep-frying and air-frying, respectively (Fig. 1J). On the contrary, anthocyanins appeared to be quite stable during deep-frying (decrease of 27.3%) but not during air-frying, which resulted in a loss of 80.3% of anthocyanins (Fig. 1K).

3.3. *Effect of deep-frying and air-frying on red-skinned onion phenolic compounds bioaccessibility*

Cooking treatments, including frying, induced a matrix softening effect, resulting in cell wall disruption, which ultimately resulted in an increased release of the phenolic compounds during gastro-intestinal digestion (*i.e.* bioaccessibility) (Cattivelli et al., 2021; De Santiago et al., 2018; Juániz et al., 2016b; Juániz et al., 2017; Martini et al., 2021). Despite the importance of the topic, no studies have been carried out to compare the bioaccessibility of phenolic compounds after deep-frying or air-frying.

As reported in Table 3, the amount of total phenolic compounds released after *in vitro* digestion was significantly different among the samples. Raw red-skinned onion showed the lowest amount of bioaccessible total phenolic compounds (60.2 ± 0.8 μmol/100 g of onion), followed by deep-fried onion (112 ± 4 μmol/100 g of onion) and air-fried onion (206 ± 1 μmol/100 g of onion). This last sample also displayed the highest bioaccessibility index (89.6% of total phenolic compounds released after digestion), significantly higher than the bioaccessibility index of deep-fried (60.5% of total phenolic compounds released after digestion) and raw (38.6% of total phenolic compounds released after digestion) red-skinned onion (Table 3).

The low bioaccessibility of total phenolic compounds in the raw red-skinned onion was almost totally due to the poor bioaccessibility of quercetin aglycone. The amount of quercetin detected after *in vitro* digestion of raw onion was 75.3 μmol/100 g of onion less than the amount extracted with the methanol/water/formic acid solution, accounting for the 78.4% of the missing total phenolic compounds after *in vitro* digestion (Table 3). The reason could be related to the poor extractability during *in vitro* digestion of quercetin strongly linked to onion macromolecules and/or to the low solubility of quercetin in hydrophilic media (Pérez-Jiménez and Saura-Calixto, 2015; Riva et al., 2019). Moreover, a small amount of released quercetin may have also undergone oxidative degradation as depicted by the increase or the appearance of di-hydroxybenzoic acid isomers, which are well-known quercetin degradation products (Fuentes et al., 2017; Rogozinska and Biesaga, 2020). In addition to quercetin, also quercetin-3-*O*-glucoside-4'-*O*-glucoside was detected in *in vitro* digested raw onion in amounts lower than that found in the extract (bioaccessibility index of 68.4%), whereas quercetin-4'-*O*-glucoside was characterized by the highest bioaccessibility (87.4%) (Table 3).

As reported in Table 3, both quercetin-3-*O*-glucoside-4'-*O*-glucoside and quercetin-4'-*O*-glucoside displayed very low bioaccessibility (16.2% and 11.5%, respectively) in deep-fried red skinned-onion samples. So much so that at the end of the *in vitro* digestion their amount was lower than that detected in the digested raw sample. However, a high amount of quercetin aglycone was detected in the digested deep-fried samples with a bioaccessibility index of over 100% (Table 3). This could be due both to the presence of oil that increased quercetin solubility and stability during digestion and/or to the matrix softening effect, as a result of the thermal treatments, that made quercetin more easily released during *in vitro* digestion (Ortega et al., 2009; Palermo et al., 2014; Zhao et al., 2019). Moreover, the bioaccessibility index above 100% indicated the occurrence of hydrolysis at the expense of quercetin-glucosides. Some previous studies found that quercetin-glucosides may be hydrolysed to the corresponding aglycone during *in vitro* digestion of apple, onion and pure compounds (Fernández-Jalao et al., 2020; Fernández-Jalao et al., 2021; Xie et al., 2022). The hydrolysis of quercetin-glucosides previously reported in apples and onions primarily occurred during gastric digestion under acidic conditions (Fernández-Jalao et al., 2020; Fernández-Jalao et al., 2021). Indeed, the authors found differences between the hydrolysis rates in untreated samples compared to the high-pressure treated samples, which displayed higher quercetin-glucoside hydrolysis during *in vitro* digestion (Fernández-Jalao et al., 2020; Fernández-Jalao et al., 2021). In a previous study carried out with yellow-skinned and red-skinned onions, the authors found a bioaccessibility index well below 100% for both quercetin-3-*O*-glucoside-4'-*O*-glucoside and quercetin-4'-*O*-glucoside after deep-frying and *in vitro* digestion suggesting the possible occurrence of quercetin-hexoside hydrolysis (Cattivelli et al., 2021). However, the authors failed to identify the quercetin aglycone in the *in vitro* digested sample (Cattivelli et al., 2021). This discrepancy may be due to the different chromatographic conditions and instruments used for the identification and quantification of phenolic compounds (low-resolution mass spectrometry *vs* high-resolution mass spectrometry utilized in this study). A similar behaviour was observed also for isorhamnetin derivatives (Table 3).

Indeed, oxidative degradation of quercetin and quercetin-mono-hexosides also occurred during *in vitro* digestion as demonstrated by the recovery well above 100% of di-hydroxybenzoic acids and di-hydroxybenzoic acid-hexosides, which are well-known degradation products of quercetin and quercetin-mono-hexosides (Cattivelli et al., 2021; Fuentes et al., 2017; Rogozinska and Biesaga, 2020).

Considering the three most important flavonols, a high bioaccessibility index was calculated for quercetin-3-*O*-glucoside-4'-*O*-glucoside, quercetin-4'-*O*-glucoside and quercetin aglycone in digested air-fried red-skinned onion. A recovery of 101% and 92.3% was

observed for quercetin and quercetin-3-*O*-glucoside-4'-*O*-gluoside, whereas for quercetin-4'-*O*-glucoside the bioaccessibility index was slightly lower (71.9%). This high recovery rate was probably due to the matrix softening effect caused by the thermal treatment. Similarly, as observed in the deep-fried samples, quercetin-glucoside hydrolysis as well as quercetin and quercetin-mono-hexoside oxidative degradation also occurred during *in vitro* digestion of air-fried red-skinned onion, as demonstrated by the appearance of oxidative products (*i.e.* di-hydroxybenzoic acids and di-hydroxybenzoic acid-hexosides). Therefore, it can be speculated that the amount of bioaccessible quercetin-derivatives was a balance between hydrolysis of the glycosidic group and oxidative degradation.

The other two most important classes of phenolic compounds in red-skinned onion, hydroxycinnamic acids and anthocyanins, were both characterized by a low bioaccessibility index (16.0% and 2.8%) after *in vitro* digestion of raw red-skinned onion. In accordance, previous studies found a low bioaccessibility index for hydroxycinnamic acids and anthocyanins in other products subjected to *in vitro* digestion (Cattivelli et al., 2021; D'Antuono et al., 2015; Fernández-Jalao et al., 2020; Martini et al., 2021). Moreover, also in deep-fried onion, anthocyanins were characterized by a low bioaccessibility index of 1.9%. However, in the case of hydroxycinnamic acids, deep-frying resulted in a significantly higher bioaccessibility compared to the raw sample (51.0% in deep-fried onion *vs* 16% in raw sample) suggesting that the thermal treatment may enhance the digestive extractability of hydroxycinnamic acids. Furthermore, in the air-fried samples, both anthocyanins and hydroxycinnamic acids displayed a higher bioaccessibility than that observed in raw and deep-fried digested onion. In particular, hydroxycinnamic acids showed a bioaccessibility index of about 100%.

The low bioaccessibility of hydroxycinnamic acids in raw red-skinned onion samples compared to the fried onion seemed therefore related to the matrix softening effect induced by the thermal treatments that favoured the extraction of hydroxycinnamic acids during digestion or protected them from degradation. Previous studies found that thermal treatments enhanced the bioaccessibility of hydroxycinnamic acids in cardoon, green pepper and eggplant (Juániz et al., 2016b; Juániz et al., 2017; Martini et al., 2021). However, we can not exclude that some oxidative degradation may occur during *in vitro* digestion. At slightly alkaline pH such as found in the intestine, hydroxycinnamic acids are readily oxidized to the related quinone, which may then react with proteins or undergo polymerization (Rawel et al., 2000).

The low bioaccessibility of anthocyanins can be attributable to the formation of the colourless chalcone pseudobase occurring at slightly alkaline pH, which resulted in the chemical degradation of the anthocyanin structure (McDougall et al., 2005).

4. Conclusions

This study compared the effect of traditional deep-frying and the most recent air-frying technology on the stability and gastro-intestinal release of phenolic compounds in red-skinned onion. Both the frying treatments affected the phenolic profile of red-skinned onion from a quantitative and qualitative point of view. In comparison with the raw sample, an increase in phenolic compounds was found for both treatments but was more pronounced after air-frying than after deep-frying. The increase of phenolic compounds was mainly a consequence of the water loss observed during frying, however, air-frying better prevented the degradation of phenolic compounds during the thermal treatment. After *in vitro* digestion, air-fried onion released the highest amount of phenolic compounds that also displayed the highest bioaccessibility index. Thereby, air-frying treatment may display health benefits not only associated with a lower amount of fats and polar toxic compounds, but also an increased release of phenolic compounds during digestion. Since the effect of thermal treatments on phenolic compound stability and bioaccessibility strongly depend on the food matrix and the phenolic structure, the presented data can not be generalized. Further studies aimed at comparing the effect of deep-frying and air-frying on phenolic compound stability and bioaccessibility by using different food matrices are strongly requested to give a more complete picture of the possible health benefits of air-frying. Anyway, these reported results enforce the possibility of exploring air-frying as a healthier alternative to deep-frying for cooking vegetable foods.

Financial support

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

Alice Cattivelli: Conceptualization, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration. **Adele Di Lorenzo:** Formal analysis, Investigation, Data curation, Writing – review & editing. **Angela Conte:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – review & editing. **Serena Martini:** Conceptualization, Validation, Investigation, Data curation, Writing – review & editing. **Davide Tagliazucchi:** Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

The authors acknowledge the Fondazione Cassa di Risparmio di Modena for funding the UPLC-ESI-Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer system at the Centro Interdipartimentale Grandi Strumenti (CIGS).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.105024.

References

Ambra, R., Lucchetti, S., Pastore, G., 2022. A review of the effects of olive oil-cooking on phenolic compounds. Molecules 27, 661.

Bahadoran, Z., Mirmiran, P., Momenan, A.A., Azizi, F., 2017. Allium vegetable intakes and the incidence of cardiovascular disease, hypertension, chronic kidney disease, and type 2 diabetes in adults: a longitudinal follow-up study. J. Hypertens. 35, 1909–1916.

Brodkorb, A., Egger, L., Alminger, M., Alvito, P., Assunção, R., Ballance, S., Bohn, T., Bourlieu-Lacanal, C., Boutrou, R., Carrière, F., Clemente, A., Corredig, M., Dupont, D., Dufour, C., Edwards, C., Golding, M., Karakaya, S., Kirkhus, B., Le Feunteun, S., Lesmes, U., Macierzanka, A., Mackie, A.R., Martins, C., Marze, S., McClements, D.J., Ménard, O., Minekus, M., Portmann, R., Santos, C.N., Souchon, I., Singh, R.P., Vegarud, G.E., Wickham, M.S.J., Weitschies, W., Recio, I., 2019. INFOGEST static in vitro simulation of gastrointestinal food digestion. Nat. Protoc. 14, 991–1014.

Cattivelli, A., Conte, A., Martini, S., Tagliazucchi, D., 2021. Influence of cooking methods on onion phenolic compounds bioaccessibility. Foods 10, 1023.

Cattivelli, A., Conte, A., Martini, S., Tagliazucchi, D., 2022. Cooking and in vitro digestion modulate the anti-diabetic properties of red-skinned onion and dark purple eggplant phenolic compounds. Foods 11, 689.

D'Antuono, I., Garbetta, A., Linsalata, V., Minervini, F., Cardinali, A., 2015. Polyphenols from artichoke heads (*Cynara cardunculus* (L.) subsp. *scolymus* Hayek): in vitro bio-accessibility, intestinal uptake and bioavailability. Food Funct. 6, 1268–1277.
De Santiago, E., Pereira-Caro, G., Moreno-Rojas, J.M., Cid, C., De Peña, M.P., 2018. Digestibility of (poly)phenols and antioxidant activity in raw and cooked cactus cladodes (*Opuntia ficus-indica*). J. Agric. Food Chem. 66, 5832–5844.
De Santiago, E., Gill, C.I.R., Carafa, I., Tuohy, K.M., De Peña, M.P., Cid, C., 2019. Digestion and colonic fermentation of raw and cooked *Opuntia ficus-indica* cladodes impacts bioaccessibility and bioactivity. J. Agric. Food Chem. 67, 2490–2499.
Fabbri, A.D.T., Crosby, G.A., 2016. A review of the impact of preparation and cooking on the nutritional quality of vegetables and legumes. Int. J. Gastron. Food Sci. 3, 2–11.
Fernández-Jalao, I., Balderas, C., Sánchez-Moreno, C., De Ancos, B., 2020. Impact of an in vitro dynamic gastrointestinal digestion on phenolic compounds and antioxidant capacity of apple treated by high-pressure processing. Innov. Food Sci. Emerg. Technol. 66, 102486.
Fernández-Jalao, I., Balderas, C., Calvo, M.V., Fontecha, J., Sánchez-Moreno, C., De Ancos, B., 2021. Impact of high-pressure processed onion on colonic metabolism using a dynamic gastrointestinal digestion simulator. Metabolites 11, 262.
Fuentes, J., Atala, E., Pastene, E., Carrasco-Pozo, C., Speisky, H., 2017. Quercetin oxidation paradoxically enhances its antioxidant and cytoprotective properties. J. Agric. Food Chem. 65, 11002–11010.
Harris, S., Brunton, N., Tiwari, U., Cummins, E., 2015. Human exposure modelling of quercetin in onions (*Allium cepa* L.) following thermal processing. Food Chem. 187, 135–139.
Juániz, I., Ludwig, I.A., Huarte, E., Pereira-Caro, G., Moreno-Rojas, J.M., Cid, C., De Peña, M.P., 2016a. Influence of heat treatment on antioxidant capacity and (poly) phenolic compounds of selected vegetables. Food Chem. 197, 466–473.
Juániz, I., Ludwig, I.A., Bresciani, L., Dall'Asta, M., Mena, P., Del Rio, D., Cid, C., De Peña, M.P., 2016b. Catabolism of raw and cooked green pepper (*Capsicum annuum*) (poly)phenolic compounds after simulated gastrointestinal digestion and faecal fermentation. J. Funct. Foods 27, 201–213.
Juániz, I., Ludwig, I.A., Bresciani, L., Dall'Asta, M., Mena, P., Del Rio, D., Cid, C., De Peña, M.P., 2017. Bioaccessibility of (poly)phenolic compounds of raw and cooked cardoon (*Cynara cardunculus* L.) after simulated gastrointestinal digestion and fermentation by human colonic microbiota. J. Funct. Foods 32, 195–207.
Koszucka, A., Nowak, A., 2019. Thermal processing food-related toxicants: A review. Crit. Rev. Food Sci. Nutr. 59, 3579–3596.
Kothari, D., Lee, W.D., Kim, S.K., 2020. Allium flavonols: Health benefits, molecular targets, and bioavailability. Antioxidants 9, 888.
Lombard, K., Peffley, E., Geoffriau, E., Thompson, L., Herring, A., 2005. Quercetin in onion (*Allium cepa* L.) after heat-treatment simulating home preparation. J. Food Compos. Anal. 18, 571–581.
Makris, D.P., Rossiter, J.T., 2001. Domestic processing of onion bulbs (*Allium cepa*) and asparagus spears (*Asparagus officinalis*): Effect on flavonol content and antioxidant status. J. Agric. Food Chem. 49, 3216–3222.
Marotti, M., Piccaglia, R., 2002.). Characterization of flavonoids in different cultivars of onion (*Allium cepa* L.). J. Food Sci. 67, 1229–1232.
Martini, S., Tagliazucchi, D., Minelli, G., Lo Fiego, D.P., 2020. Influence of linseed and antioxidant-rich diets in pig nutrition on lipid oxidation during cooking and in vitro digestion of pork. Food Res. Int. 137, 109528.
Martini, S., Conte, A., Cattivelli, A., Tagliazucchi, D., 2021a. Domestic cooking methods affect the stability and bioaccessibility of dark purple eggplant (*Solanum melongena*) phenolic compounds. Food Chem. 341, 128298.
Martini, S., Cattivelli, A., Conte, A., Tagliazucchi, D., 2021b. Black, green, and pink pepper affect differently lipid oxidation during cooking and *in vitro* digestion of meat. Food Chem. 350, 129246.
McDougall, G.J., Fyffe, S., Dobson, P., Stewart, D., 2005. Anthocyanins from red wine-their stability under simulated gastrointestinal digestion. Phytochemistry 66, 2540–2548.
Ortega, N., Reguant, J., Romero, M.P., Macià, A., Motilva, M.J., 2009. Effect of fat content on the digestibility and bioaccessibility of cocoa polyphenol by an in vitro digestion model. J. Agric. Food Chem. 57, 5743–5749.
Palermo, M., Pellegrini, N., Fogliano, V., 2014. The effect of cooking on the phytochemical content of vegetables. J. Sci. Food Agric. 94, 1057–1070.
Patil, B.S., Pike, L.M., Hamilton, B.K., 1995. Changes in quercetin concentration in onion (*Allium cepa* L.) owing to location, growth stage and soil type. N. Phytol. 130, 349–355.
Pellegrini, N., Fogliano, V., 2017. Cooking, industrial processing and caloric density of foods. Curr. Opin. Food Sci. 14, 98–102.
Pérez-Burillo, S., Rufián-Henares, J.A., Pastoriza, S., 2019. Effect of home cooking on the antioxidant capacity of vegetables: relationship with Maillard reaction indicators. Food Res. Int. 121, 514–523.
Pérez-Jiménez, J., Saura-Calixto, F., 2015. Macromolecular antioxidants or non-extractable polyphenols in fruit and vegetables: intake in four European countries. Food Res. Int. 74, 315–323.
Price, K.R., Bacon, J.R., Rhodes, M.J.C., 1997. Effect of storage and domestic processing on the content and composition of flavonol glucosides in onion (*Allium cepa*). J. Agric. Food Chem. 45, 938–942.
Ramírez-Anaya, J.D.P., Castañeda-Saucedo, M.C., Olalla-Herrera, M., Villalón-Mir, M., Serrana, H.L., Samaniego-Sánchez, C., 2019. Changes in the antioxidant properties of extra virgin olive oil after cooking typical Mediterranean vegetables. Antioxidants 8, 246.
Rawel, H.M., Kroll, J., Riese, B., 2000. Reactions of chlorogenic acid with lysozyme: physicochemical characterization and proteolytic digestion of the derivatives. J. Food Sci. 65, 1091–1098.
Riva, A., Ronchi, M., Petrangolini, G., Bosisio, S., Allegrini, P., 2019. Improved oral absorption of quercetin from Quercetin Phytosome®, a new delivery system based on food grade lecithin. Eur. J. Drug Metab. Pharmacokinet. 44, 169–177.
Rogozinska, M., Biesaga, M., 2020. Decomposition of flavonols in the presence of saliva. Appl. Sci. 10, 7511.
Rohn, S., Buchner, N., Driemel, G., Rauser, M., Kroh, L.W., 2007. Thermal degradation of onion quercetin glucosides under roasting conditions. J. Agric. Food Chem. 55, 1568–1573.
Rinaldi de Alvarenga, J.F., Quifer-Rada, P., Francetto Juliano, F., Hurtado-Barroso, S., Illan, M., Torrado-Prat, X., Lamuela-Raventós, R.M., 2019. Using extra virgin olive oil to cook vegetables enhances polyphenol and carotenoid extractability: A study applying the sofrito technique. Molecules 24, 1555.
Rodrigues, A.S., Pérez-Gregorio, M.R., García-Falcón, M.S., Simal-Gándara, J., 2009. Effect of curing and cooking on flavonols and anthocyanins in traditional varieties of onion bulbs. Food Res. Int. 42, 1331–1336.
Santos, C.S.P., Cunha, S.C., Casal, S., 2017. Deep or air frying? A comparative study with different vegetable oils. Eur. J. Lipid Sci. Technol. 119, 1600375.
Seal, C.J., de Mul, A., Eisenbrand, G., Haverkort, A.J., Franke, K., Lalljie, S.P.D., Mykkänen, H., Reimerdes, E., Scholz, G., Somoza, V., Tuijtelaars, S., van Boekel, M., van Klaveren, J., Wilcockson, S.J., Wilms, L., 2008. Risk-benefit considerations of mitigation measures on acrylamide content of foods – a case study on potatoes, cereals and coffee. Br. J. Nutr. 99, S1–S46.
Tian, J., Chen, J., Lv, F., Chen, S., Chen, J., Liu, D., Ye, X., 2016. Domestic cooking methods affect the phytochemical composition and antioxidant activity of purple-fleshed potatoes. Food Chem. 197, 1264–1270.
Van Boekel, M., Fogliano, V., Pellegrini, N., Stanton, C., Scholz, G., Lalljie, S., Somoza, V., Knorr, D., Jasti, P.R., Eisenbrand, G., 2010. A review on the beneficial aspects of food processing. Mol. Nutr. Food Res. 54, 1215–1247.
Wan, Q., Li, N., Du, L., Zhao, R., Yi, M., Xu, Q., Zhou, Y., 2019. Allium vegetable consumption and health: An umbrella review of meta-analyses of multiple health outcomes. Food Sci. Nutr. 7, 2451–2470.
Williamson, G., 2017. The role of polyphenols in modern nutrition. Nutr. Bull. 42, 226–235.
Xie, L., Deng, Z., Zhang, J., Dong, H., Wang, W., Xing, B., Liu, X., 2022. Comparison of flavonoid *O*-glycoside, *C*-glycoside and their aglycones on antioxidant capacity and metabolism during in vitro digestion and in vivo. Foods 11, 882.
Zaghi, A.N., Barbalho, S.M., Guiguer, E.L., Otoboni, A.M., 2019. Frying process: from conventional to air frying technology. Food Rev. Int. 35, 763–777.
Zhao, C., Liu, Y., Lai, S., Cao, H., Guan, Y., Cheang, W.S., Liu, B., Zhao, K., Miao, S., Riviere, C., Capanoglu, E., Xiao, J., 2019. Effects of domestic cooking process on the chemical and biological properties of dietary phytochemicals. Trends Food Sci. Technol. 85, 55–66.