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EFFECT OF COOKING ON YELLOW ONION QUERCETIN

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Flavonoids are bioactive secondary plant metabolites with a range of beneficial effects on human health. Consumption of a diet rich in these compounds might decrease the risk of circulatory and inflammatory diseases and certain cancers. Onions are a good source of quercetin derivatives with the major constituents quercetin-3,4'-glucoside and quercetin-4'-glucoside, which are not deglucosylated during cooking. There is a gradient in flavonoid content from outer to inner scales in raw onion and the former remain the richest even after cooking. Over 50% of flavonoids and soluble plant material are readily transferred from onion into soup during cooking. Cooking may increase the total amount of flavonoids available by disrupting the plant tissue and rendering better accessible.

INTRODUCTION

Flavonoids are polyphenolic secondary plant metabolites occurring in a variety of foods. Over 6,500 flavonoids have been described so far and classified into several subclasses: flavones, flavonols, flavanones, isoflavones, flavanols (including catechins and tannins) and anthocyanins. In plants, they function as protection against UV radiation, pathogens and herbivores [Harborne & Williams, 2000; Ross & Kasum, 2002] and are located mainly in aerial parts [Aherne & O'Brien, 2002], predominantly as β-O-glycosides.

There is an increasing awareness of the role of flavonoids as epidemiological studies suggest that consumption of flavonol- and isoflavone-rich diets might decrease the risk of developing coronary heart disease and certain cancers [Formica & Regelson, 1995; Arai *et al.*, 2000]. Five out of seven studies showed a negative correlation between flavonol intake and the development of cardiovascular disease and the protective effect of flavonols seems to be rather systemic than local [Hollman, 2001].

Onion is one of the richest and commonly consumed sources of dietary flavonoids with quercetin ranging from traces in white to 2.5-3 mmol/kg in red varieties [Tsushida & Suzuki, 1996; Price & Rhodes, 1997]. Yellow onions were reported to contain about 0.7-1 mmol/kg quercetin derivatives [Tsushida & Suzuki, 1996; Makris & Rossiter, 2001]. Quercetin is concentrated in the skin of most onions where it imparts the yellow brown colour. This non-edible dry peel is richer in total flavonoids compared to edible flesh, which are mainly present as aglycones due to flavonol deglucosylation during peel formation [Tsushida & Suzuki, 1996]. Two major flavonoids of onion skin are quercetin aglycone and quercetin-4'-glucoside [Suh *et al.*, 1999]. The onion flesh contains a wide range of quercetin, isorhamnetin and kaempferol derivatives in varying proportions [Bilyk *et al.*, 1984] with an increasing trend in the content of quercetin glucosides from the inner to outer scales [Patil & Pike, 1995; Tsushida & Suzuki, 1996].

In edible part of onion bulbs, quercetin was identified as -4'-O-β-glucoside, -3,4'-diO-β-glucoside (Figure 1), -3-O-β--glucoside, -7-O-β-glucoside, -3,7-diO-β-glucoside, -7,4'-diO--β-glucoside [Park & Lee, 1996; Price & Rhodes, 1997], the former two being the major constituents. Quercetin aglycone was detected in long stored onions but only at levels less than 2% of the total quercetin [Price & Rhodes, 1997].

Flavonoids are generally found at higher concentrations in outer layers of fruits and vegetables [Tsushida & Suzuki, 1996], therefore peeling results in their great loss. After homelike peeling red onions contained 79% of the original total content of quercetin-4'-glucoside and only 27% of the anthocyanins [Gennaro *et al.*, 2002]. Quercetin-3,4'-diglucoside (Q3,4'Glc) and quercetin-4'--glucoside (Q4'Glc) were unaffected by chopping of onions [Makris & Rossiter, 2001].

Usual food preparation conditions did not lead to complete loss of the two major glucosides in onions and the food contained a mixture of the two glycosides (Q3,4'Glc, Q4'Glc) and a variable amount of the quercetin aglycone. However, Q3,4'Glc was rapidly degraded in macerated tissues with a 50% loss after 5 h resulting in production of

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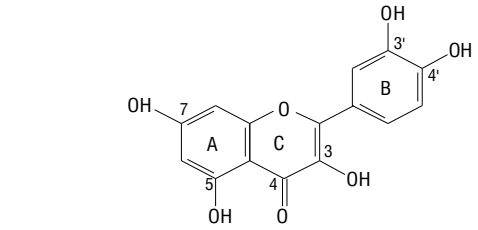
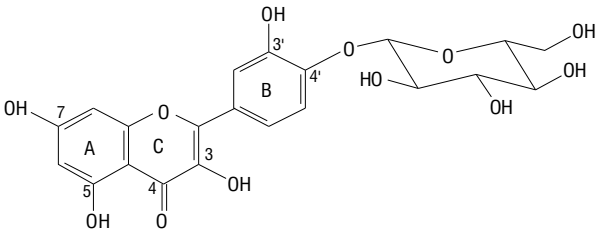
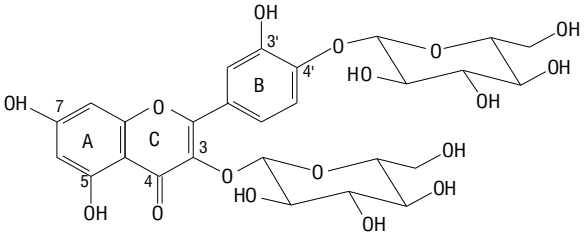


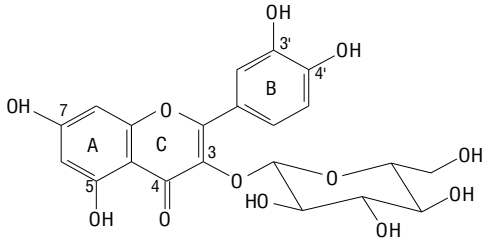
Quercetin



Quercetin-4'-*O*-β-glucoside (Spiraeoside)



Quercetin-3,4'-di*O*-β-glucoside



Quercetin-3-*O*-β-glucoside (Isoquercitrin)

FIGURE 1. Structures of polyhydroxylated flavonoid quercetin and its glucosides present in onion bulb.

quercetin monoglycoside and aglycone [Price & Rhodes, 1997], which could be explained by the activity of onion flavonol glucosidases [Tsushida & Suzuki, 1996].

Quercetin glycosides were not degraded when onion was cooked for 40 min, but they were transferred into the cooking water. The total flavonoid content in onion remained unaltered during frying. Microwave heating for 1 min resulted in 50% increase of total quercetin content probably due to their better extractability during determination procedure [Ioku *et al.*, 2001].

Flavonoid glucosides seem to resist thermal degradation, and the β-glucosidases capable of hydrolysing glucosides are probably degraded during heat-treatment. However, the amount of flavonoids available may increase during technological processing, *e.g.* by release from food matrix. Moreover, there is a flavonoid concentration gradient from outer to inner layers. We were interested in further exploration of the sites where the changes occur during cooking of onion.

MATERIALS AND METHODS

Materials & Chemicals

In the experiments, yellow onion purchased from a local supermarket (Olsztyn, Poland), was used. Formic acid, acetonitrile, acetic acid, and methanol were of HPLC grade obtained from Sigma. Flavonoid standards: quercetin (Sigma-Aldrich, St. Louis, USA), quercetin-3-glucoside (Extrasynthese, Genay, France), quercetin-3,4'-O-glucoside and quercetin-4'-O-glucoside (generous gifts from Dr. T. Tsushida, National Food Research Institute, Tsukuba, Japan) were prepared as methanol stock solutions (stored at -20°C) and diluted to required concentrations with, methanol/acetic acid (95/5, v/v). Flavonoid concentrations in samples were calculated using the corresponding standard calibration curves.

General equipment. UV-visible spectrophotometer UV-1601PC (Shimadzu, Japan); centrifuges 5415R MiniSpin (Eppendorf AG, Germany), MPW-360 (Poland), and GS-15R (Beckman); homogeniser (Janke & Kunkel, IKA® Labortechnik, UltraTurrax T25 with S25N-8G dispersing tool, Germany); Sonics vibracell T.M (Sonics & Materials, USA); HPLC 10AD System with UV detector SPD-10A (Shimadzu, Japan; λ=360 nm).

Methods

Homelike onion processing. Onion bulbs were peeled off dry skin to the first whole fresh scale, cut into 4-6 mm cubes and a 150-g aliquots were either left fresh as raw controls, or fried or boiled. Frying was conducted without oil on a pre-heated frying pan for 3 min with shaking to prevent sample over-heating and burning. In cooking experiment, onion and 100 mL of water were boiled for 30 min in a boiling flask under reflux.

Onion boiling experiment. To follow the overall changes of the quercetin in the onion due to cooking in water as well as the changes within particular sections of the onion, the bulb was longitudinally cut into quarters, two of which were cooked and two left as relevant controls. The onion wedges for cooking were wrapped in cheesecloth pockets to prevent them from falling apart while processed. First wedge was cooked as one piece while the second after separation into 3 sections was put in three pockets but cooked together. Sections were: outer layer (first outer onion scale), middle part (next 4-5 scales under the outer layer depending on the size of particular bulb) and remaining section was called inner layer. Samples were boiled in water 5-times the onion weight for 30 min under reflux. Cooking was performed in a three-neck boiling flask allowing taking 2 mL soup sub--samples at 5, 10, 15, and 30 min. Sub-samples were spun (MiniSpin, 12 000 x g; 5 min) and the 0.5 mL supernatant aliquots were freeze-dried. After cooking, soups (liquids) and onion solids were separated, soups were filtered through filter paper (Filtrak, Jena, Germany) and all the samples were freeze-dried.

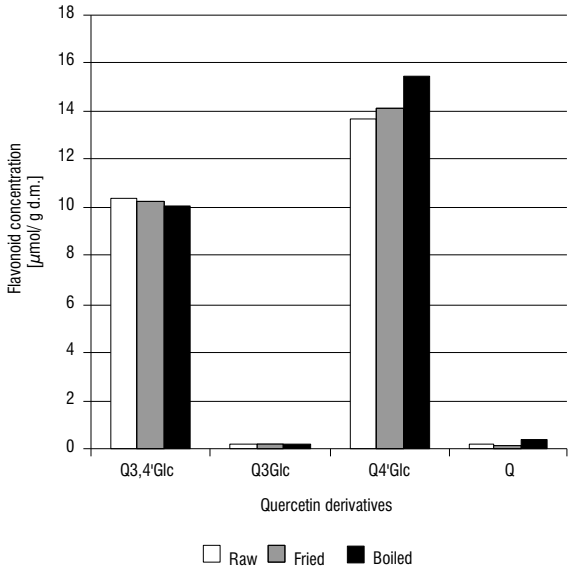


FIGURE 2. Effect of processing on flavonoid concentration (μmol) per g of dry matter (d.m.): cooking increased the Q4'Glc concentration.

Experiment with onion outer layers. Onion bulb was cut longitudinally into quarters and four pieces of the outer scale were separated. One piece was used to equally balance the weight of remaining 3 quarters used in the experiment: raw control and two for cooking. Onion samples were cut into smaller pieces (but not chopped) in order to fit them into boiling flasks. The same procedure was applied for the control sample immediately prior to freezing. Cooking was done for 30 min under reflux at water:onion ratio of 5:1 (w/w). One quarter after boiling was freeze-dried with the soup whereas in case of the other quarter, solids and soup liquid were freeze-dried and analysed separately.

Flavonoid extraction. Lyophilised onion samples were pulverised and (an aliquot) used for flavonoid extraction. Flavonoids originating from soup were extracted directly from the test tube in which the soup sub-sample was freeze--dried. Dry material was extracted 5 times (solvent added, vortex 1 min, sonication 1 min, repeated 3 times, spun at 12 000 x g, 3 min); extracts were combined and filled up to known volume. The solvent for extraction was 80% methanol/acetic acid, (95/5 v/v).

Analysis of onion quercetin derivatives on HPLC-UV. Extracts were filtered (0.2 μm, Millipore) and injected (5 μL) on reversed-phase C18(2) LUNA 3μ column, 150 x 2 mm, (Phenomenex) at 35°C. Solvents A (0.05% formic acid/water, v/v) and B (acetonitrile) were run at 0.2 mL/min using a gradient of 14% B increasing to 24% B (14 min), 37% B (30 min), 80% B (1 min), hold on at 80% B (5 min), and then decreasing to 14% B (1 min), hold on at 14% B (19 min).

RESULTS AND DISCUSSION

Homelike onion processing

The first experiment indicated the difference in two ways of homelike onion processing on changes in quercetin derivatives concentration (Figure 2). Frying did not change its total content, whereas boiling seemed to increase the total flavonoid content in dry matter, probably due to their better release from the thermally disrupted plant matrix. This increase can be attributed to better accessibility of flavonoids by the extraction solvent, *i.e.* flavonoids were probably better extractable from dry matter originating from boiled onion. Thus, the apparent gain most likely originated in poorer extraction yields from raw onions. It is probable that this improved accessibility can also influence the bioavailability of quercetin from cooked onion since processed food matrix may be better accessible by digestion media. Ioku *et al.* [2001] microwaved the onion and observed also an increase in total quercetin content (by 50%), but not after 40-min cooking.

Onion boiling experiment

There is a gradient of flavonoid content from outer to inner layers in raw onion [Patil & Pike, 1995; Tsushida

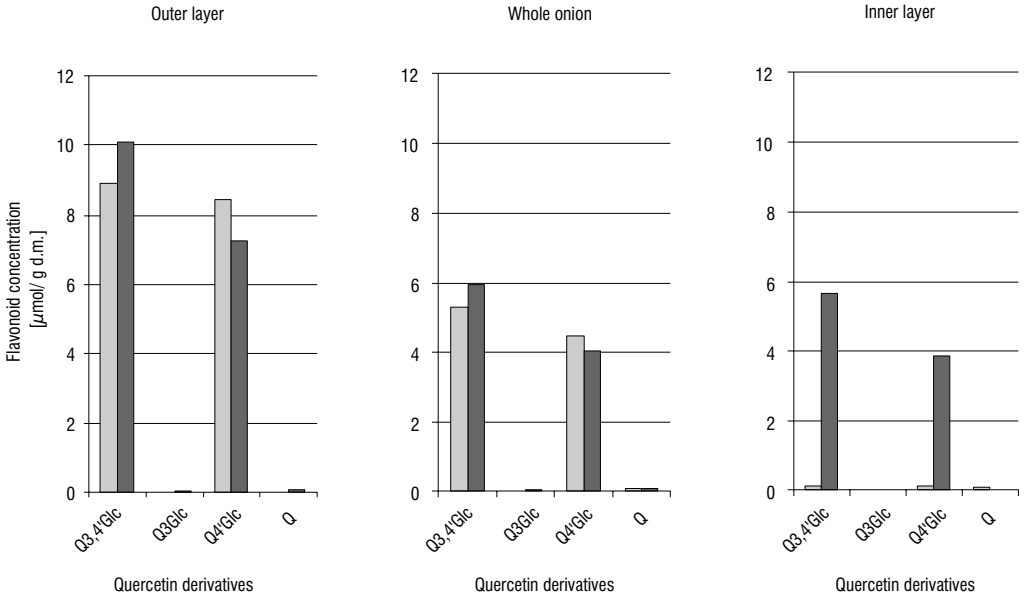


FIGURE 3. Comparison of quercetin derivatives concentration in outer, inner layers and the whole onion before (□) and after cooking (■).

& Suzuki, 1996]. Therefore, here, we were interested not only in the overall changes of quercetin derivatives in onion due to cooking, but also in these changes within the particular sections of onion bulb (Figure 3). In raw material, the concentrations of total quercetin derivatives were 0.30 μmol/g d.m. and 17.30 μmol/g d.m. in inner and outer layers, respectively. Total average flavonoid concentration in the whole raw onion was 9.85 μmol/g d.m., and this again increased due to cooking. The poorest - inner layer was markedly enriched, presumably with flavonoids previously washed out from other layers and transferred through the soup (Figure 4). The final concentrations of Q3,4'Glc and Q4'Glc in inner layer were comparable to those in whole cooked onion. Most surprisingly, the richest, outer onion scale contained even higher concentration of some flavonoids (Q3,4'Glc, quercetin) after boiling (Figure 3). Flavonoids were washed out from the outer layer, still the total concentration per dry weight in cooked outer layer was comparable to that in untreated sample (17.3 and 17.4 μmol/g d.m. in raw and treated outer layers, respectively). This apparent increase can be only in part attributed to the release of quercetin from onion matrix. One have to keep in mind that during onion cooking there is intensive washing out of soluble components and what is left from onion after cooking is of different quantity and quality. The analysis of soup subsamples revealed a rapid transfer of Q3,4'Glc and Q4'Glc from onion to water, reaching more than the half of the final flavonoid soup concentration during the first 15 min of cooking (Figure 4). To clarify this phenomenon an experiment with outer onion scales cooking was done and quercetin and mass transfer were followed.

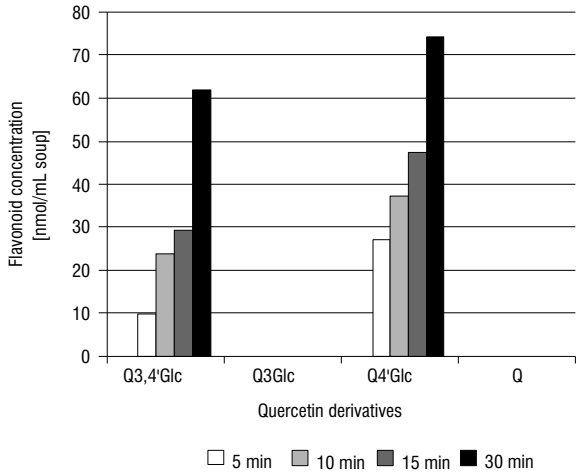


FIGURE 4. Transfer of quercetin derivatives into soup during cooking.

Experiment with onion outer layers

Comparing the onion parts, outer layers were found to have the highest concentration of the two major quercetin derivatives, Q3,4'Glc and Q4'Glc, and because of that may serve as a good source of flavonoids. Therefore, the outer layer is the most important part of onion from the soup enrichment in quercetin point of view. In the experiment, onion outer layers were cooked with the same water/onion ratio as in previous experiments. After cooking, when solids and soup were analysed as a whole, the total flavonoid content increased by 25% and so were the concentrations of both major constituents (Q3,4'Glc, Q4'Glc) and this may be due to the changes in onion matrix. Separation of the solids from the liquid showed that as much as 59% of the quercetin derivatives and 54% of dry matter initially present in the onion outer layers were transferred into the liquid during 30-min cooking what made soup a good source of dietary flavonoids (Figure 5). However, free quercetin was found in onion solids only, what may correspond to its poor solubility in water and/or stronger binding to plant structures than its glycosidic forms.

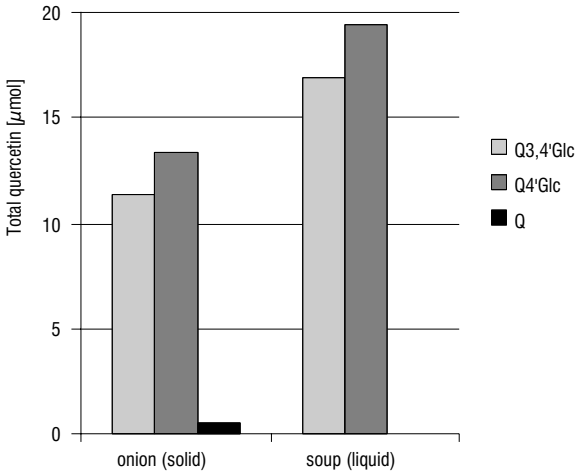


FIGURE 5. Distribution of quercetin derivatives between solids and soup after cooking of onion.

CONCLUSIONS

Presumably even more material and flavonoids would be transferred into soup if higher than 5-times water to onion ratio was used. Such higher ratio is typical of domestic soup preparation and would justify the tradition that in some kitchens the cooked onion is discarded (after it had supplied the flavonoids to the soup). Finally, beneficial health effects associated with high intake of flavonoids on one side and a very high content of quercetin in onion outer scales on the other points to necessity of minimal onion peeling during food preparation.

ACKNOWLEDGEMENTS

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