Domestic Processing of Onion Bulbs (*Allium cepa*) and Asparagus Spears (*Asparagus officinalis*): Effect on Flavonol Content and Antioxidant Status

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Two commonly consumed plant foods, onion bulbs and asparagus spears, were subjected to typical domestic processing, including chopping, maceration, and boiling. The impact of these processes on flavonol content was assessed. Further, the consequences of these processes on the antioxidant capacity of the tissues were evaluated with the β-carotene bleaching method. Chopping significantly affected rutin content in asparagus, yielding an 18.5% decrease in 60 min; but in onions, quercetin 3,4′-diglucoside (Q_{DG}) and quercetin 4′-glucoside (Q_{MG}) were virtually unaffected by chopping. Boiling for 60 min had more severe effects, as it caused overall flavonol losses of 20.6 and 43.9% in onions and asparagus, respectively. Chopping of tissues did not considerably influence the antioxidant capacity, but boiling did provoke notable changes.

Keywords: *Antioxidant capacity; asparagus spears; boiling; chopping; flavonols; onion bulbs*

INTRODUCTION

Flavonols are of widespread occurrence in the most common edible fruits, vegetables, and seeds (*1*, *2*), and their content may reach up to a few hundred mg kg^{-1} of fresh weight (*3*). Berries such as bog whortleberry (*Vaccinium uliginosum*) and cranberry (*Vaccinium oxycoccos*) have been found to contain 184 and 263 mg kg^{-1} fresh weight of total flavonols, respectively (*4*). Certain vegetables, however, such as onions (*Allium cepa* L.) and kale (*Brassica oleracea* L. cv. Alba DC.), could be considered as exceptional dietary sources, as their content in total flavonols may reach 349 and 311 mg kg^{-1} fresh weight, respectively, determined as aglycons (*5*).

As flavonols constitute an integral part of the human diet, some effort has been expended on the determination of flavonol levels that are consumed daily by humans. Early estimations (*6*) showed the daily average intake of total flavonoids to be about 1.0 g, with 115 mg being the share of flavonols and flavones. Recently, the "Seven Countries Study" (*7*) revealed that total daily flavonoid intake may vary from 2.6 to 68.2 mg, with the percentage of quercetin being 39−100%. In another study on 17 volunteers from 14 countries, mean consumption of quercetin and kaempferol was found to be approximately 28 mg/day (*8*).

The investigations on the effects of flavonoid-containing plant foods have been based, to a great extent, on a limited number of epidemiological studies. In these studies the flavonoid (mainly flavone and flavonol) content of commonly consumed plant foods and products was used as a crucial factor in estimating the average daily flavonoid intake. However, food composition tables, which are necessary tools for epidemiological and nutritional studies, have been created on the basis of analytical data from raw plant tissues, and thus they actually represent the composition of foodstuffs only in their raw state. Environmental variables and processing may affect to a significant extent the concentrations and biological activities of flavonoids, and these factors have not been taken into consideration. This aspect, nevertheless, is of great importance, considering that only a small amount of fruits and vegetables are consumed in their raw state, whereas most of them need to be processed for safety, quality, and economic reasons.

There are very few recent research studies on the impact of common domestic and industrial processing practices on flavonoid composition of plant foods, and it appears that there are some noteworthy discrepancies in the conclusions that have been drawn. As regards flavonols in particular, common domestic processes such as boiling, frying, and microwave cooking can lower quercetin concentrations in onions and tomatoes by 35−82% (*9*). An overall loss of 25% in quercetin glucosides in onions following frying and boiling has also been reported (*10*), and quercetin 4′-glucoside and quercetin 3,4′-diglucoside content in onions was reportedly decreased by more than 50% after 25 min of boiling (*11*). Moreover, blanching has been found to reduce quercetin and kaempferol levels in onions by 39 and 64%, respectively (*12*), and myricetin and quercetin in sweet potato leaves by 19 and 50%, respectively (*13*). However, no significant losses in flavonol content were observed when Swiss chard (*14*), broccoli florets (*15*), and green beans (*16*) were subjected to boiling.

The present research was undertaken in order to clarify the impact of regular domestic processing on the flavonol content of two commonly consumed plant foods, as well as the role of structural features on flavonol degradation. On the basis of the results obtained,

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assumptions were made regarding the parameters concerned with flavonol thermal decomposition during boiling, on the basis of data from model systems (*17*, *18*).

MATERIALS AND METHODS

Chemicals. Water used for HPLC analyses was distilled, purified by EasyPure RT ultrapure water system, and filtered through 0.45-μm filters (Millipore). Acetic acid, acetonitrile (MeCN), chloroform, methanol (MeOH), and trifluoroacetic acid (TFA) were from BDH Chemicals Ltd. (Poole, England). MeCN and TFA were HPLC grade. All other solvents were analar grade. *trans*-β-Carotene, linoleic acid, quercetin, rutin (quercetin 3-*O*-rhamnosylglucoside), and Tween 20 were from Sigma Chemical Co. (St. Louis, MO). Citric acid and trichloroacetic acid (TCA) were from BDH Chemicals Ltd. (Poole, England). Quercetin 4′-*O*-glucoside (Q_{MG}) and quercetin 3, 4′-*O*-diglucoside (Q_{DG}) were kindly provided by Mark Bennett (Imperial College at Wye, University of London). Orange-skinned onions (*Allium cepa*) and asparagus spears (*Asparagus officinalis*) were purchased from a local food store in Wye, Kent, U.K.

Boiling. The outer dry layers of onion were manually removed, and the bulb was cut longitudinally into two pieces. The pieces were weighed and one piece was immediately wrapped in muslin and boiled for 60 min in 400 mL of tap water, pH 6.98−7.04. The other piece was used as a control sample.

Chopping. Onion bulbs were skinned and cut longitudinally into two pieces. The pieces were weighed, and one piece was immediately chopped carefully into small pieces (approximately 0.5-cm length) with a sharp knife. Samples were allowed to stand at room temperature, under open air, for 60 min. The opposite piece was used as control.

In both cases asparagus spears were treated similarly. For each treatment, four onion bulbs and four asparagus spears ($n = 4$) were used.

Sample Preparation for HPLC Analysis (Onions). Tissues were extracted three times with 80 mL of 80% aqueous MeOH in a domestic electric blender. The samples were filtered through muslin and Whatman no. 1 filter paper, under vacuum. 30% TCA (0.5 mL) was added and the mixture was concentrated to approximately 10 mL with a rotary vacuum evaporator ($T \leq 40$ °C). The concentrate was made up to 25 mL with MeOH, spun down, and filtered through Millex syringe filters (0.45 μm). Boiled samples and water were treated similarly.

Sample Preparation for HPLC Analysis (Asparagus). Fresh tissues were extracted as described for onion bulbs. The extracts were pooled and concentrated to approximately 10 mL. The aqueous concentrate was extracted twice with 20 mL of chloroform to remove chlorophyll and then concentrated nearly to dryness. The residue was made up to 25 mL with MeOH, spun down, and filtered through 0.45-μm Millex syringe filters (Millipore).

Analytical HPLC Procedure. A Waters 600E gradient pump with an Applied Biosystems 757 detector set at 260 nm, were used. The system was interfaced by JCL 6000 software. Chromatography was carried out on a Waters Symmetry C_{18}, 3.9 × 150 mm, 5 μm column, with a Waters guard column packed with the same material. Columns were thermostatically controlled to maintain a temperature of 40 °C. Eluents were (A) 0.1% aqueous TFA (pH 2.3) and (B) 0.1% TFA in MeCN/water (6:4), and the flow rate was 1 mL min^{-1}. Injection was made by a Rheodyne injection valve with 20-μL fixed loop. Following is the elution program used: 100% A to 60% A in 40 min, 60% A to 50% A in 10 min, 50% A to 30% A in 10 min, and then isocratic elution for another 10 min. The column was washed with 100% MeCN and reequilibrated with 100% eluent A before the next injection. Quantitation of Q_{DG}, Q_{MG}, rutin, and quercetin was made using an external standard. Standard solutions were prepared in EtOH and kept at −20 °C.

Determinations of Iron and Copper. Total iron and copper concentrations were determined in the tap water used for boiling treatment. Both determinations were performed by atomic absorption using a Pye Unicam SP 9 spectrophotometer. Wavelengths employed for the analyses were 258.3 and 324.8 nm, for iron and copper, respectively. In both cases, calibration curves were established using solutions with concentrations varying from 0.5 to 5.0 mg L^{-1}.

Evaluation of Antioxidant Capacity. For the evaluation of antioxidant capacity, the well-established method of thermally induced β-carotene bleaching was used, as described previously (*19*, *20*). In a 100-mL, round-bottom flask, 0.02 mL of linoleic acid, 0.2 mL of Tween 20, 1.0 mL of *trans*-β-carotene (0.2 mg mL^{-1} in chloroform), and 0.2 mL of sample, were added, and the mixture was taken to dryness with nitrogen. To the resulting residue, 50 mL of oxygenated distilled water was added and mixed, and the absorbance was read at 470 nm. The solution was then incubated in a water bath at 50 °C to induce autoxidation. Samples were taken at 10-min intervals to monitor the evolution of A_{470}. Flasks were covered with aluminum foil throughout experiments to avoid light-induced oxidation of β-carotene. Each experiment was repeated twice.

Antioxidant potency was based upon three different parameters.

First Parameter. Antioxidant activity (A_A) was determined as percent inhibition relative to control sample (*21*):

$$A_A = [(R_{control} - R_{sample})/(R_{control})] \times 100 \qquad (a)$$

where $R_{control}$ and R_{sample} represent the bleaching rates of β-carotene without and with the addition of antioxidant, respectively. Degradation rates (R_D) were calculated according to first-order kinetics:

$$R_D = ln(A_I/A_X) \times 1/t \qquad (a\text{-}1)$$

where *ln* is natural log, A_I is the initial A_{470} ($t = 0$), and A_X is the A_{470} at $t = 10$, 20, 30, etc., min.

Second Parameter. The oxidation rate ratio (R_{OR}) was calculated by:

$$R_{OR} = R_{sample}/R_{control} \qquad (b)$$

where R_{sample} and $R_{control}$ are as described previously (*22*).

Third Parameter. The antioxidant activity coefficient (C_{AA}) was calculated using:

$$C_{AA} = [(A_{s(120)} - A_{c(120)})/(A_{c(0)} - A_{c(120)})] \times 1000 \qquad (c)$$

where $A_{s(120)}$ is the absorbance of the sample containing antioxidant at $t = 120$ min, $A_{c(120)}$ is the absorbance of the control at $t = 120$ min, and $A_{c(0)}$ is the absorbance of the control at $t = 0$ min.

Statistics. Values represent means of four individual experiments ($n = 4$). Standard deviation values are also given. Differences in the antioxidant capacities of onion and asparagus extracts were calculated using Student's test at a 5% significance level. Differences in the antioxidant capacities of onion extracts were correlated with Q_{DG}:Q_{MG} ratios using linear regression analysis.

RESULTS

Processing of Onion Bulbs. *Effect on Flavonol Content*. Changes in flavonol content of onion bulbs after each treatment were measured by means of HPLC. The extraction method employed gave very satisfactory yields of flavonol recovery, ranging from 96 to 99%. A typical chromatogram of methanolic onion extract is illustrated in Figure 1a. The two major flavonol glucosides, quercetin 3,4′-diglucoside (Q_{DG}) and quercetin 4′-glucoside (Q_{MG}), can easily be distinguished as they are the most abundant flavonoids in onions and represent

Table 1. Effect of Domestic Processes on Flavonol Content of Onion Bulbs[a]

	treatment					
	chopping			boiling		
compound[b]	control	chopped	% (↑↓)[c]	control	boiled	% (↑↓)
Q_{DG}	308.2 ± 12.6	301.0 ± 9.2	2.3 (↓)	294.8 ± 13.5	270.0 ± 14.1	8.4 (↓)
Q_{MG}	224.5 ± 5.5	226.2 ± 9.0	0.8 (↑)	208.0 ± 7.9	129.7 ± 5.8	37.6 (↓)
Q	3.8 ± 1.0	3.9 ± 0.4	3.7 (↑)	1.4 ± 0.2	0.8 ± 0.1	43.2 (↓)
total	536.4	531.1	1.0 (↓)	504.2	400.5	20.6 (↓)

[a] Values are expressed as mg kg^{-1} fresh weight and represent means of duplicate analysis of four individual experiments ($n = 4$) ± SD. [b] Q_{DG}, quercetin 3,4′-diglucoside; Q_{MG}, quercetin 4′-glucoside; Q, free quercetin. Q_{DG} and Q_{MG} were determined as rutin. [c] Symbols (↑) and (↓) indicate increase and decrease in content, respectively.

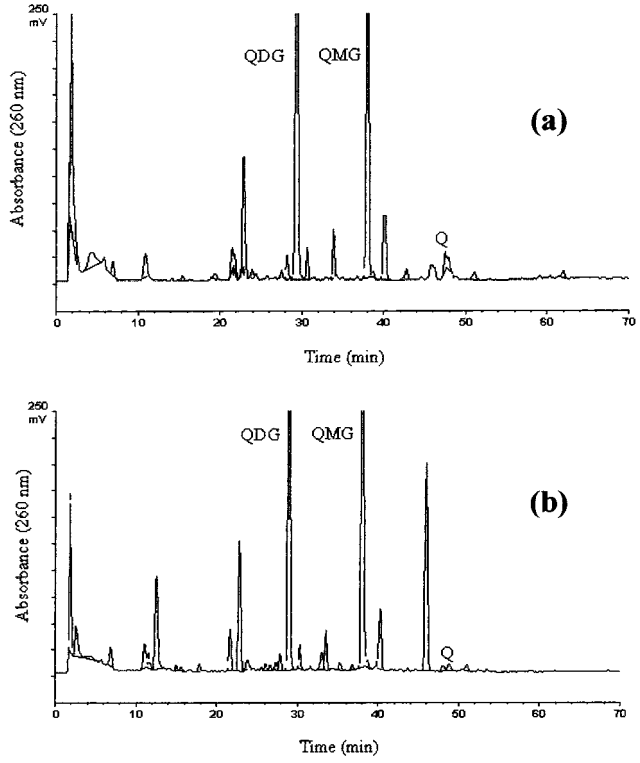

Figure 1. (a) Typical chromatogram of a methanolic onion extract. Q_{DG}, quercetin 3,4′-diglucoside; Q_{MG}, quercetin 4′-glucoside. Q, quercetin. Detection was accomplished at 260 nm. (b) Trace of cooking water after boiling of onion bulbs, showing principal flavonol glucosides and the peaks with retention time 12 and 46 min, which were not detected in control samples.

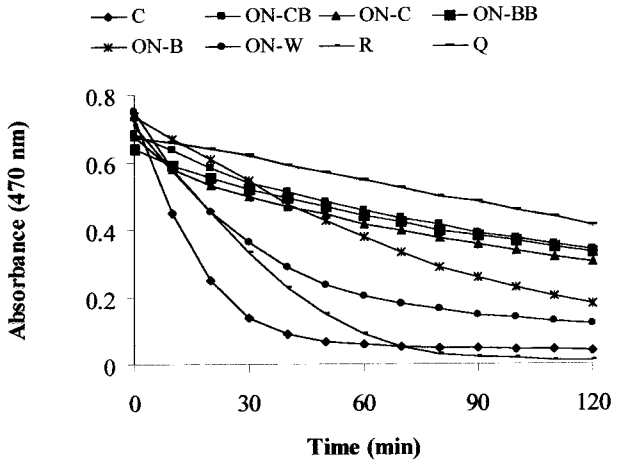

Figure 2. Bleaching rates of β-carotene as affected by onion extracts. C, control; ON−CB, control sample (chopping). ON−C, sample which underwent chopping; ON−BB, control sample (boiling); ON−B, sample which underwent boiling; ON−W, water after boiling of plant tissue; R, rutin; Q, quercetin. All samples contained flavonols at a final concentration of 10.5 μg mL^{-1}.

approximately 80% of the total flavonol content (*23*). Rutin and isorhamnetin 4′-glucoside (*24*) along with quercetin 3,7,4′-triglucoside (*25*) are another three flavonol conjugates that may accompany Q_{DG} and Q_{MG}, while some other quercetin and kaempferol derivatives may occur as minor constituents (*2*).

Quantitative determination of Q_{DG} and Q_{MG} showed that the content of these two components varied from 294.8 to 308.2 and 208 to 224.5 mg kg^{-1} of fresh weight, respectively (Table 1). Free quercetin was also found to occur at 1.4−3.8 mg kg^{-1} of fresh weight. Chopping of onion bulbs, which was followed by a 60-min maceration, resulted in a decrease in Q_{DG} content, with concomitant increase in Q_{MG} and quercetin. Particularly, Q_{DG} content declined by 2.3%, whereas the corresponding increases for Q_{MG} and quercetin were 0.8 and 3.7%. Overall, a negligible loss of 1% was found.

Boiling of bulbs, however, considerably affected the content of Q_{DG}, Q_{MG}, and quercetin, yielding losses of 8.4, 37.6, and 43.2%, respectively, with the overall loss being 20.6%. The individual analyses also showed that 36.4% of Q_{DG} and 22.7% of Q_{MG} leached into the cooking water, while quercetin was detected only in the cooking water. The ratio Q_{DG}:Q_{MG} in the boiled tissue was 2.24 and in the water was 4.37, indicating that leaching of Q_{DG} was favored.

The HPLC profile of the extracts from the chopped tissues did not present any notable difference compared to that obtained from the control samples. However, the analysis of the cooking water revealed the appearance of two distinct peaks with retention times of approximately 12 and 46 min (Figure 1b), which were not encountered among the peaks of control samples, suggesting the formation of new products that absorb at 260 nm. The nature of these products remains obscure, but it could be speculated that their formation might be associated with flavonol breakdown. It should be noted that these two components were not detected in the extracts from boiled bulbs.

Effect on Antioxidant Status. Onion extracts containing 10.5 μg mL^{-1} of total flavonols (Q_{DG} + Q_{MG}) were tested for antioxidant ability. For comparison, quercetin and rutin were also examined (Figure 2), and on the basis of β-carotene bleaching rates three parameters for each sample were calculated (Table 2). The aglycon quercetin was found to be a remarkable antioxidant, but its corresponding 3-rutinoside, rutin, was by far less effective. Extracts deriving from unprocessed onion bulbs (ON−CB, ON−BB) also exhibited very high antioxidant potency compared to extracts from either chopped or boiled tissues and cooking water, with

Table 2. Parameters Used to Evaluate the Antioxidant Properties of Onion Extracts, Obtained before and after Each Processing[a]

sample	parameters		
	A_A[b]	R_{OR}[c]	C_{AA}[d]
control	0.00	1.0000	0.00
quercetin	91.50	0.0850	533.24
rutin	19.80	0.8020	−44.80
ON−CB	83.05	0.1695	429.19
ON−C	77.68	0.2233	377.18
ON−BB	84.53	0.1548	417.63
ON−B	75.58	0.2743	200.88
ON−W	47.93	0.5208	111.27

[a] Extracts and pure compounds were tested at a final concentration of 10.5 μg mL^{-1}. ON−CB, control sample (chopping); ON−C, sample which underwent chopping; ON−BB, control sample (boiling); ON−B, sample which underwent boiling. All samples contained flavonols at a final concentration of 10.5 μg mL^{-1}. ON−W: Water after boiling of plant tissue. [b] Antioxidant activity. [c] Oxidation rate ratio. [d] Antioxidant activity coefficient.

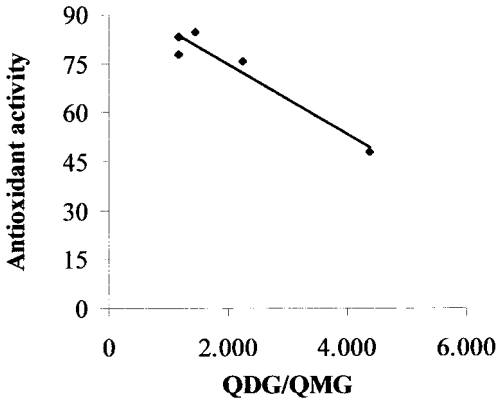

Figure 3. Correlation between Q_{DG}/Q_{MG} and antioxidant activity (A_A) of onion extracts.

respect to all three parameters. In contrast, the lowest values were obtained from boiled tissues and cooking water. With the exception of A_A values, rutin was significantly less effective from its aglycon and all the extracts ($P < 0.05$).

Because all extracts had the same flavonol concentration, the significant differences observed for rutin, along with the slight differences between control and processed samples, led to an attempt to distinguish possible structure−activity relationships. When A_A values were plotted against Q_{DG}/Q_{MG} ratios (Figure 3), a very high correlation was found ($r^2 = 0.9270$) between low ratios and increased A_A, indicating that the antioxidant properties of extracts were strongly related to Q_{MG} content. This correlation was even higher ($r^2 = 0.9919$) when R_{OR} was used instead of A_A values, but poorer though still significant ($r^2 = 0.7681$) for C_{AA} values.

Processing of Asparagus Spears. *Effect on Flavonol Content.* A typical trace of an asparagus methanolic extract is shown in Figure 4a. Rutin was the predominant peak, but at least five other minor peaks were also detected, which may represent other quercetin and kaempferol glycosides (*2*). Unlike onions, however, no quercetin was found and it could be said that in asparagus spears rutin is not accompanied by its aglycon. Quantitative analysis of extracts gave a rutin content of 274.1 to 286.5 mg kg^{-1} of fresh weight.

Chopping of spears resulted in a considerable decrease in rutin content, which reached 18.5% (Table 3).

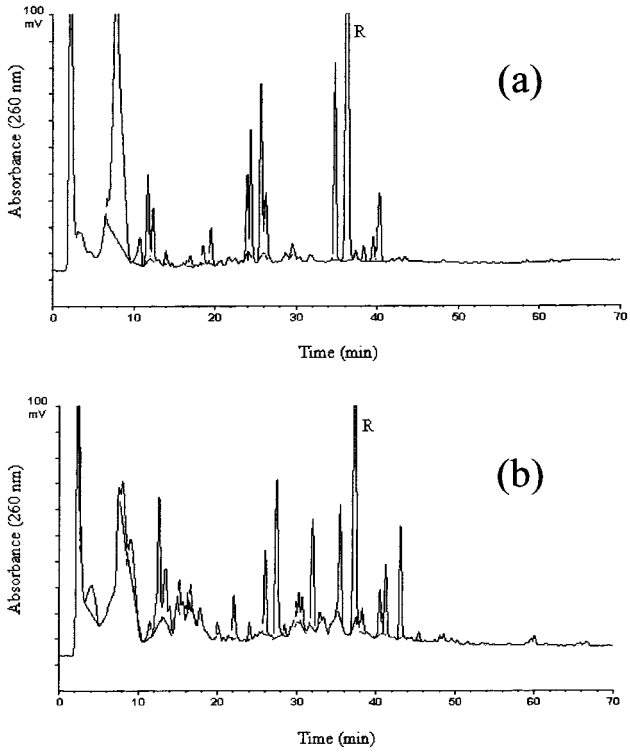

Figure 4. (a) Typical chromatogram of methanolic asparagus extracts. Detection was performed at 260 nm. R, rutin. (b) HPLC trace of cooking water used for asparagus boiling. The appearance of some small peaks not detected in control samples can be seen. Monitoring was carried out at 260 nm. R, rutin.

However, this decrease was not translated into quercetin formation, as the HPLC profile of the extracts from chopped tissues did not present any notable difference from that of control sample. Contrary to that, boiling of asparagus tissues that yielded a rutin decomposition of 43.9% was shown to generate a series of small peaks not encountered in the control sample (Figure 4b). Most of these peaks had shorter retention times than that of rutin, a finding that suggests the formation of more polar peaks, in terms of a reversed-phase HPLC system. These peaks were either significantly smaller, on the basis of peak area, or completely absent from extracts of boiled tissue. 30.4% of rutin leached into the cooking water, but in this instance too, no quercetin could be detected.

Effect on Antioxidant Status. Figure 5 illustrates the bleaching rates of β-carotene that were recorded with respect to addition of individual extracts. Since rutin is the major flavonoid constituent in asparagus spears that possesses antioxidant activity, it could be reasonably expected that the extracts exhibit activities comparable to this flavonol. On the basis of the values given in Table 4, it can be seen that indeed all the extracts tested gave lower but statistically insignificant different values, except in the case where comparison was carried out with A_A values. In this instance the extract deriving from boiled tissues (termed AS−B) presented considerably weaker antioxidant potency ($P < 0.05$) when compared to that of either rutin or the other extracts. Quercetin was once again the most efficient of all samples. Cooking water was not tested because it was found to contain very low levels of rutin.

Table 3. Effect of Domestic Processes on Rutin Content of Asparagus.

	treatment					
	chopping			boiling		
compound	control	chopped	% (↑↓)[b]	control	boiled	% (↑↓)
rutin	286.5 ± 6.0	233.6 ± 3.5	18.5 (↓)	274.1 ± 3.8	153.7 ± 5.5	43.9 (↓)
quercitin	nd[c]	nd		nd	nd	
total	286.5	233.6	18.5 (↓)	274.1	153.7	43.9 (↓)

[a] Values are expressed as mg kg^{-1} fresh weight and represent means of duplicate analysis of four individual experiments ($n = 4$) ± SD. [b] (↑) and (↓) indicates increase and decrease in content, respectively. [c] Not detected.

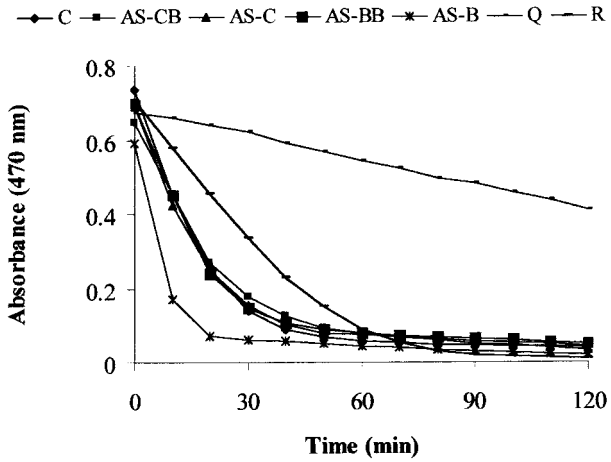

Figure 5. Effect of asparagus extracts on β-carotene bleaching rate. C, control; AS−CB, control sample (chopping). AS−C, sample which underwent chopping; AS−BB, control sample (boiling); AS−B, sample which underwent boiling; R, rutin; Q, quercetin. All samples contained rutin at a final concentration of 10.5 μg mL^{-1}.

Table 4. Parameters Used to Evaluate the Antioxidant Properties of Asparagus Extracts, Obtained Before and After Each Processing

	parameters		
sample	A_A[a]	R_{OR}[b]	C_{AA}[c]
control	0.00	1.0000	0.00
quercetin	91.50	0.0850	533.24
rutin	19.80	0.8020	−44.80
AS−CB[d]	17.68	0.8233	2.89
AS−C	6.53	0.9348	−10.12
AS−BB	10.4	0.8960	13.00
AS−B	−35.53	1.3553	−31.79
AS−W[e]			

[a] Antioxidant activity. [b] Oxidation rate ratio. [c] Antioxidant activity coefficient. [d] AS−CB, control sample (chopping). AS−C, sample which underwent chopping; AS−BB, control sample (boiling); AS−B, sample which underwent boiling. All samples contained rutin at a final concentration of 10.5 μg mL^{-1}. AS−W, water after boiling of plant tissue. [e] Not tested.

DISCUSSION

Impact of Processing on Flavonol Content of Tissues. Onions contain two abundant quercetin glucosides, which are conjugated at different sites of the flavonol skeleton. In Q_{DG} glucose is attached to 3 and 4′-position, but in Q_{MG} glucose occupies the 4′-position. Total mean flavonol content of onion bulbs was found to be 520.3 mg kg^{-1} of fresh weight, in accordance with previously published data giving average flavonol contents of 378 (*26*), 385 (*5*), 409.5 (*9*), and 410 (*12*) mg kg^{-1} of fresh weight. Higher values of 1187 (*10*), 942.8 (*27*), and 933.5 (*28*), and as low as 65 (*29*) and 170 (*30*) mg kg^{-1} of fresh weight have also been reported.

Chopping and subsequent maceration for 60 min provoked only minor changes to both glucoside and quercetin concentrations. It appears, therefore, that common domestic practices may not enable significant transformations, probably because longer time periods are required for enzyme action. Maceration of onion tissues has been shown to result in an important decrease in Q_{DG} concentration after 5 h, whereas complete disappearance required 24 h (*28*). However, even after such a prolonged maceration, losses in total flavonols were rather low, varying from 10.7 to 17.7%. The increases observed in Q_{MG} and quercetin content appeared to occur at the expense of Q_{DG}, indicating hydrolysis of the latter conjugate. This finding is in agreement with previous studies (*28*), which demonstrated that decreases in Q_{DG} could be quantitatively explained by increases in Q_{MG} and quercetin content.

Previously published data on green asparagus indicated that rutin content may account for 0.02 to 0.1% (w/w) (*31*). Indeed, the quantitative data from asparagus extracts gave a mean content of 280.30 mg kg^{-1} of fresh weight. Chopping and maceration caused a decrease in rutin content as high as 18.5%, but the fact that this decline was not accompanied by liberation of quercetin might suggest that rutin was oxidatively cleaved, rather than hydrolyzed. However, hydrolysis might occur to some extent, but quercetin was oxidized as soon as it was liberated from the sugar, and thus it did not accumulate to detectable amounts.

Processing of tissues by boiling had more severe effects in terms of flavonol loss. The 60-min treatment resulted in 20.5 and 43.9% decrease in total flavonol content for onions and asparagus, respectively, and it was also observed that boiling extracted a considerable amount of conjugates into the cooking water. Previous findings showed that boiling of onion rings for 60 min gave an approximately 80% decrease for Q_{MG}, but Q_{DG} was virtually unaffected (*11*). Boiling for 15 min has been reported to reduce quercetin content in onions by 75% (*9*), but other investigations gave a 25% decrease in flavonol content when onions were boiled for 10 min (*10*). It has been supported, however, that boiling of onions does not result in any appreciable quercetin loss (*12*).

In onions, Q_{DG} exhibited the lowest loss (8.4%), whereas Q_{MG} and quercetin contents declined by 37.6 and 43.2%, respectively. According to observations on model systems (*17*, *18*), either at pH 13.0 or 8.0, the 3-position as well as the catechol structure in B-ring are two important sites on the flavonol skeleton that confer instability. Thus, Q_{DG}, in which these two positions are blocked, showed much greater stability than Q_{MG}, in which the 3-position is not conjugated. This phenomenon was even more profoundly expressed in quercetin, which has both sites exposed. Although no iron or copper ions were detected in the cooking water, it is not known whether trace metals had any contribution to flavonol disappearance, as previously proposed

(*18*) due to analytical data on trace metal content of onion tissues.

Rutin content in asparagus spears exhibited a more extended decline compared to that of Q_{DG} and Q_{MG} in onions, a fact that could be attributed to the different substitution pattern. It could be said that the occupation of the 3-position in rutin does not have such a stabilizing effect as does conjugation at the corresponding 4′-position in Q_{MG}, with respect to boiling. However, the results may not be absolutely comparable, because of qualitative and quantitative differences of the plant tissues.

Impact of Processing on the Antioxidant Status of Plant Tissues. The antioxidant potency of a given plant food may be ascribed to an array of compounds that occur naturally in plants, such as phenols, ascorbic acid, carotenoids, alkaloids, and terpenoids (*32*). Recent evidence, however, strongly suggests that the antioxidant ability of plant foods and products may be attributed, to a great extent, to their content of compounds of flavonoid nature (*13*, *33*−*38*). Processing of plant foods may have a prominent impact on their antioxidant activity (*39*), but the accurate effect of processing on the overall antioxidant potential cannot be predicted. This is due to the fact that, during processing, loss of antioxidants or formation of compounds with pro-oxidant action may lower the antioxidant capacity. On the other hand, alterations to the structure of the existing antioxidants, as well as the formation of novel antioxidant components may enhance the initial antioxidant status (*40*−*42*). Thus the influence of processing may be positive, negative, or none.

In the case of onions, flavonols remained virtually intact during maceration, and thus the impact on the antioxidant potential was trivial. Boiling of onion bulbs caused considerable changes to flavonols, both in terms of quantity and relative amounts, and this was reflected to some extent in the antioxidant potential, which was lower, although not statistically significant, in boiled tissue and cooking water. The differences observed were highly correlated with the Q_{DG}/Q_{MG} ratio, suggesting that the higher the Q_{MG} concentration, the higher the antioxidant ability of the tissue. Because the antioxidant potency of flavonols substantially depends on the catechol group in the B-ring and the 3-hydroxyl group (*43*−*45*), it would be expected that Q_{MG} would have a greater antioxidant action than Q_{DG}, because in the latter these two basic functions are blocked. In contrast, in Q_{MG} the 3-hydroxyl group is not conjugated, and therefore it may participate in redox reactions or chelate with metal ions, thereby preventing Fenton-type reactions. The significantly lower antioxidant properties of rutin, which is conjugated at the 3-position, further confirm this. Asparagus extracts exhibited an antioxidant characteristic very similar to that of rutin, indicating that rutin content is the most important determinant. However, extracts from boiled tissues having the same rutin concentration showed pro-oxidant action, probably due to lower content of other flavonols that decomposed during processing, or because of the formation of other pro-oxidants.

CONCLUSIONS

The behavior of three characteristic flavonol glycosides occurring in common plant foods was studied with regard to regular domestic processes. It was found that treatments such as chopping might cause moderate changes to flavonol composition, but the overall impact is rather without particular importance. Contrary to that, processing involving heating may cause alterations to flavonols that cannot be overlooked, as these alterations appear to directly affect the antioxidant status of plant tissues. The modifications on flavonol structure that might occur during processing may have profound consequences on their biological properties, but because the anti/pro-oxidant capacity of plant tissues is strongly influenced by a number of factors, it is very difficult to extrapolate the effects of the consumption of processed plant foods on human health. However, it is claimed that similar studies may contribute to performing more accurate estimations on flavonoid consumption, and therefore could be used as critical parameters in assessing the actual flavonol intake from various processed foods.

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