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Flavonoid Content in Fresh, Home-Processed, and Light-Exposed Onions and in Dehydrated Commercial Onion Products

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Onion plants synthesize flavonoids as protection against damage by UV radiation and by intracellular hydrogen peroxide. Because flavonoids also exhibit health-promoting effects in humans, a need exists to measure their content in onions and in processed onion products. To contribute to the knowledge about the levels of onion flavonoids, HPLC and LC-MS were used to measure levels of seven quercetin and isorhamnetin glucosides in four Korean commercial onion bulb varieties and their distribution within the onion, in scales of field-grown onions exposed to home processing or to fluorescent light and in 16 commercial dehydrated onion products sold in the United States. Small onions had higher flavonoid content per kilogram than large ones. There was a graduated decrease in the distribution of the flavonoids across an onion bulb from the first (outside) to the seventh (innermost) scale. Commercial, dehydrated onion products contained low amounts or no flavonoids. Losses of onion flavonoids subjected to "cooking" (in percent) ranged as follows: frying, 33; sautéing, 21; boiling, 14−20; steaming, 14; microwaving, 4; baking, 0. Exposure to fluorescent light for 24 and 48 h induced time-dependent increases in the flavonoid content. The results extend the knowledge about the distribution of flavonoids in fresh and processed onions.

KEYWORDS: ***Allium cepa*; onions; onion products; HPLC; LC-MS; flavonoids**

INTRODUCTION

Onion plants (*Allium cepa*) synthesize antioxidative flavonols, a class of flavonoids, to protect the cells against damaging effects of UV radiation and hydrogen peroxide (*1*). Fresh and dehydrated onions are widely used in the human diet, not only as a spicy garnish but as a source of nutrients and non-nutritive health-promoting compounds, as reviewed in refs *2* and *3*. Worldwide production of onions is estimated at ∼64 million tons (*4*). The largest producers (in millions of tons) are China (19.8), India (5.5), the United States (3.4), Turkey (2.2), South Korea (1.8), and Japan (1.6). Components of onions (in percent) include water (89.1), carbohydrates (9.3), protein (1.1), fat (0.1), vitamins, minerals, sulfur compounds responsible for their pungency (*5*), saponins (*6*), and flavonoids.

Flavonoids possess numerous beneficial bioactive properties that may also benefit human health (*7*). Beneficial effects associated with one or more of the bioactive onion ingredients include anticarcinogenic, anticholesterol, antidepressant (*8*); antidiabetic, antifungal (*9*); anti-inflammatory (*10*); antimicrobial, antiosteoporosis (*11*); antioxidative, hypotensive, and antispasmodic (*12*) activities as well as an affinity for copper, iron, and zinc ions (*13*).

Because onions are one of our major food plants, the major objectives of the present study were to define and validate with the aid of HPLC and LC-MS the content and distribution of seven quercetin and isorhamnetin glucosides in 4 varieties of Korean onion bulbs, in leafy scales (layers) of an onion bulb, in small, medium, and large size onions of one variety, in scales exposed to home processing and fluorescent light, and in 16 dehydrated onion products sold at retail in the United States. **Figure 1** shows the structures of the flavonoids of the onion scales evaluated in the present study.

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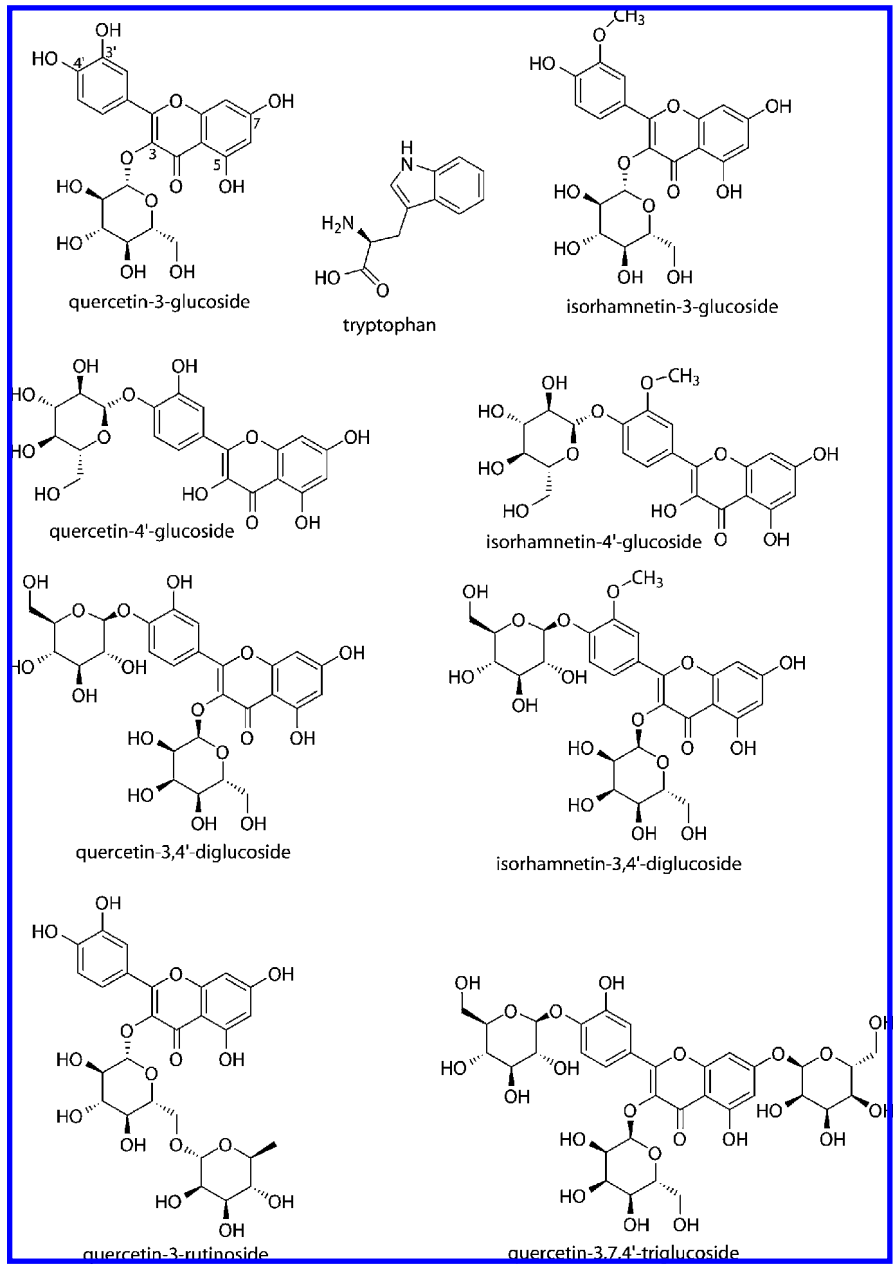

Figure 1. Structures of flavonoids and of tryptophan evaluated in the present study.

MATERIALS AND METHODS

Materials. Quercetin 3-*O*-glucoside (catalog no. 9505), isorhamnetin 3-*O*-glucoside (catalog no. 09535), and isorhamnetin 3-*O*-rutinoside (catalog no. 14201) were obtained from ChromaDex, Inc. (Irvine, CA) and quercetin 3,4′-*O*-glucoside (catalog no. 2161-1) and quercetin 4′-*O*-glucoside (catalog no. 1161-1) from Polyphenols (Sandnes, Norway). Rutin trihydrate (quercetin 3-*O*-rutinoside) (catalog no. R-9000) was obtained from Sigma (St. Louis, MO). HPLC grade acetonitrile, ethanol, and formic acid were obtained from commercial sources. The solvents were filtered through a 0.45 μm membrane filter (Millipore, Bedford, MA) and degassed in an ultrasonic bath before use. Fresh onions (var. Kaenonboll, Tubo, OP, and Red Snack) were obtained from Garak Market in Seoul, Korea. Fresh onions (var. Mansang) used for the scales study were obtained from the Agricultural Experiment Station, Gyeongnam Chang Yeong, Korea. **Table 1** lists the names and commercial sources of 16 dehydrated chopped, granulated, minced, powdered, salted, sliced, and toasted commercial onion products of unknown history sold at retail in California that were evaluated for flavonoid content.

Table 1. Commercial Onion Products Evaluated in This Study

sample	product
A	minced onions, brand X
B	minced onions, brand X
C	minced onions, brand X
D	chopped onions, brand X
E	chopped onions, brand X
F	chopped onions, brand X
G	onion powder, brand X
H	onion powder, brand X
I	onion salt, brand X
J	granulated onion with parsley, brand Y
K	sliced onions, brand Y
L	toasted onions, brand Y
M	onion powder, white and green onions with parsley, brand X
N	onion powder, brand Z
O	granulated onions, organic, brand Z1
P	minced onions, organic, brand Z2

Extraction of Flavonoids. *Onion Bulbs.* Three uniform-sized onion bulbs from four Korean varieties [Kaenonboll (white color), average wt = 266 ± 35 g, height = 86 ± 6 mm, width = 86 ± 6 mm; Tubo (white), average wt = 223 ± 2 g, height = 73 ± 4 mm, width = 79

± 3 mm; OP (white), average wt = 294 ± 10 g, height = 91 ± 8 mm, width = 87 ± 0.4 mm; Red Snack (purple), average wt = 184 ± 8 g, height = 63 ± 3 mm, width = 83 ± 2 mm] were selected for analysis of flavonoids. After removal of the outer peel, the bulbs were cut vertically with a clasp knife from the top to the basal scale; each divided side was then cut with a knife vertically to widths of 1 cm, then to smaller pieces, and mixed well. Each onion sample (10.00−10.80 g) was placed into a 100 mL flask containing boiling 80% ethanol (50 mL) and equipped with a reflux condenser. The samples were simmered for 5 min to stop enzymatic activity. The mixture was then homogenized in a Waring blender and centrifuged at 15000*g* for 10 min at 10 °C. The residue was extracted twice with 80% ethanol (20 mL). The combined supernatants were diluted to 100 mL with 80% ethanol. An aliquot (10 mL) was concentrated in a rotary evaporator at 30 °C. The residue was dissolved in 80% ethanol (1.0 mL). This solution was used for HPLC.

Onion Bulbs by Size. Three uniform-sized onion samples from three sizes of Tubo onion bulbs were evaluated: large size (average wt = 319 ± 2 g; height = 85 ± 9 mm; width = 92 ± 3 mm); medium size (average wt = 223 ± 2 g; height = 73 ± 41 mm; width = 79 ± 3 mm); small size (average wt = 123 ± 3 g; height = 69 ± 1 mm; width = 62 ± 4 mm). The extraction method was the same as that described for the onion bulbs.

Onion Scales. Three uniform-sized Mansang onion bulbs (average wt = 237 ± 18 g; height = 75 ± 3 mm; width = 81 ± 5 mm) were selected for analysis. The bulbs were cut vertically with a clasp knife from the top to the basal scale and divided into seven parts. Each separated scale was then cut to small pieces with a clasp knife and mixed well. Samples were extracted as previously described.

Home Processing of Onion Scales. Three uniform-sized Tubo onion bulbs (average wt = 226.6 ± 7.8 g; height = 74.7 ± 2.4 mm; width = 79.0 ± 2.3 mm) were cut vertically with a clasp knife from the top to the basal scale and then divided into seven parts. The second scale was selected for experiments on cooking effects. The scales were divided into two groups (each 5−7 g). The first was the untreated control, and the second was treated as follows:

Baking. Samples were wrapped with aluminum foil and placed for 5 min in a preheated, 200 °C gas oven range (Dongyang Magic Co., Korea).

Boiling. Samples were boiled for 5 min in 100 mL of distilled water containing 1 or 3% NaCl.

Frying. Samples were fried for 2 min, submerged in 350 mL of 100% soybean oil (Ottogi Co., Korea) heated to 150 °C.

Microwaving. Samples were placed onto the middle of a china plate and then cooked at high heat for l min in a microwave oven (Mistubishi-RO-D52, Japan).

Sautéing. Samples were chopped into pieces (0.3 cm wide and 0.5 cm long) and cooked on a stovetop in a shallow pan for 3 min in soybean oil (3 mL).

Steaming. Samples were placed in a steamer containing 500 mL of distilled water and then cooked at high heat for 5 min.

Onion Scales Exposed to Fluorescent Light. Three uniform-sized Mansang onion bulbs (average wt = 249 ± 3 g; height = 75 ± 4 mm; width = 80 ± 2 mm) were selected for the analysis. The bulbs were cut vertically with a clasp knife from the top to the basal scale and then divided into seven parts. The second and fourth scales were selected for the light experiments. The scales were divided into two groups of 5 g each. One group was wrapped with aluminum foil and the other with transparent plastic film. The samples were placed in an irradiation room at 25 °C and then irradiated with the fluorescent light (3000 lx) for two photoperiods (24 and 72 h). After irradiation, each sample was macerated in a glass mortar in 80% ethanol (10 mL) and centrifuged at 15000*g* for 10 min at 10 °C. The residue was re-extracted three times with 80% ethanol (10 mL) and centrifuged. The combined supernatants were diluted to 50 mL with 80% ethanol. An aliquot (10 mL) was then concentrated in a rotary evaporator at 30 °C. The residue was dissolved in 80% ethanol (1.0 mL) and centrifuged. This supernatant (20 μL) was used for HPLC.

Dehydrated Onion Products. All commercial onion products were finely ground into powders with a mortar and pestle or a homogenizer. Each powder (~0.60 g) was placed into a 5 mL volumetric flask to which was added 5 mL of 80% ethanol. The flask was then placed into an ultrasonic bath for 60 min. The filtrate was centrifuged at 15000*g* for 10 min at 10 °C. The extracts were then passed through a 0.45 μm Millipore nylon filter (Bedford, MA) before HPLC analysis.

HPLC. HPLC was carried out on a Hitachi liquid chromatograph model 665-II equipped with a Shimadzu UV−Vis detector (model SPD-10Avp, Kyoto, Japan) set at 280 and 340 nm. Column temperature was controlled with a Shimadzu CTO-10Asvp thermometer. Chromatogram peak areas were integrated with a Hitachi D-2500 chromatointegrator. An Inertsil ODS-3v column [5 μm, 4.0 × 250 mm (GL Science Inc., Tokyo, Japan)] was used to separate the flavonoids. The mobile phase consisted of the following linear gradient of acetonitrile (A) and 0.5% formic acid (B): 5−95% (0−5 min), 18−82% (5−30 min), 70−30% (30.1−90 min), 90−10% (90.1−100), 5−95% (100.1−120 min). The flow rate was 0.8 mL/min at 30 °C. Injection volume was 20 μL. Three separate analyses were carried out with each sample.

LC-MS/MS. Liquid chromatography−mass spectrometry experiments were performed by an ion trap mass spectrometer (LCQ, Thermo Fisher Scientific Inc.) equipped with an HPLC system (Agilent, model HP-1100, Palo Alto, CA) connected with a DAD (G1315A). The sample solution (1−5 μL) was applied on an Inertsil ODS-3 column (2.1 × 150 mm, 3 μm, GL Sciences Inc., Tokyo, Japan). It was separated at the flow rate of 0.2 mL/min by a gradient solvent system analogous to that described for HPLC. The HPLC eluate was introduced into the mass spectrometer 3 min after the sample injection. The experiments were carried out in the positive- and negative-ion modes.

Operating parameters of the mass spectrometer were as follows: ESI spray voltages, 6 kV (positive mode) and 4.5 kV (negative mode); capillary temperature, 250 °C; capillary voltages, 8 V (positive mode) and −42 V (negative mode); sheath gas (nitrogen) flow rate, 64 (arbitrary units); auxiliary gas flow rate, 55 (arbitrary units); tube lens offset voltages, −20 V (positive mode) and −15 V (negative mode); multipole 1 offset voltages, −2.25 V (positive mode) and 1.0 V (negative mode); multipole 2 offset voltages, −5.5 V (positive mode) and 7.0 V (negative mode); intermultipole lens voltages, −16 V (positive mode) and 14 V (negative mode). Helium gas was used as the collision gas, and the relative collision energy was set at 40% for MS/MS and MS^3 experiments. Ions were isolated over a selected mass window of 2 Da.

Quantification. Integrated chromatographic peak areas from the test samples were compared to peak areas of known amounts of standard flavonoids. Onion extracts were analyzed before and after the addition of known amounts of flavonoids. Recovery (%) = [(concentration of flavonoid in spiked sample)/(concentration of endogenous flavonoid + spike)] × 100.

Structure of Unidentified Substance (UIS). Multiple samples of peak 1, shown in the chromatogram of an onion extract (**Figure 2**) eluting at 17.7−18.3 min, were collected from the HPLC column. The combined samples were then dried at 20 °C under reduced pressure. The residue was dissolved in 50% aqueous methanol containing 1% acetic acid. An aliquot was analyzed for mass (molecular weight) using an ApexII 70e Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics Inc., Billerica, MA) in the positive-ion mode. ^1H and ^{13}C NMR spectra of the compound were recorded on an Avance 500 NMR spectrometer (Bruker BioSpin, Karlsruhe, Germany) in D_2O at 298 K.

RESULTS AND DISCUSSION

Analytical Aspects. HPLC retention times of authentic flavonoid standards ranged from 36.9 min for quercetin 3,4′-diglucoside to 46.2 min for quercetin 4′-glucoside (**Figure 2**). Retention times determined by LC-MS were similar to those obtained by HPLC. Recoveries of spiked samples ranged from 92.4 ± 1.3% for isorhamnetin 3-rutinoside to 101.7 ± 4.4% for quercetin 4′-glucoside. LOD values ranged from 2.6 ng for quercetin 4′-glucoside to 8.3 ng for quercetin 3-*O*-rutinoside. Calibration plots were linear at the concentration range from 0 to ~1000 ng/20 μL for all compounds (results not shown).

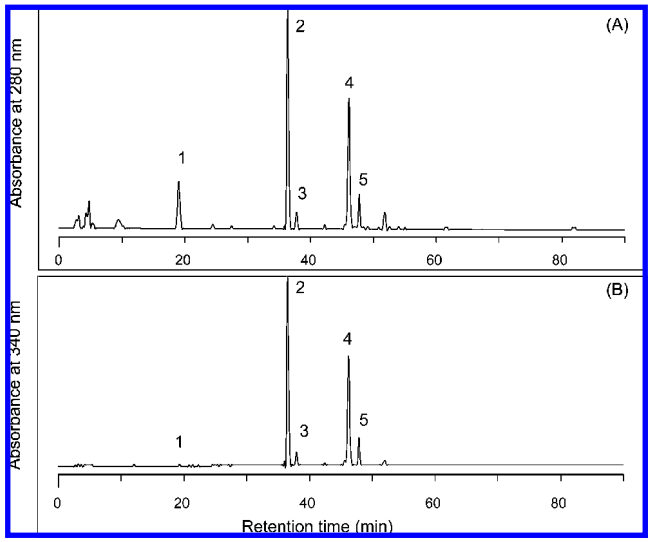

Figure 2. HPLC chromatograms of the second onion scale with detection at 280 and 340 nm. Conditions: column, Inertsil ODS-3v (5 μm, 4.0 × 250 mm); column temperature, 30 °C; mobile phase, acetonitrile/ 0.5% formic acid (gradient mode); flow rate, 0.8 mL/min. Peaks: 1, tryptophan; 2, quercetin 3,7,4′-triglucoside; 3, quercetin 7,4′-diglucoside; 4, quercetin 3,4′-diglucoside; 5, isorhamnetin 3,4′-diglucoside; 6, quercetin 3-glucoside; 7, quercetin 4′-glucoside; 8, isorhamnetin 4′-glucoside.

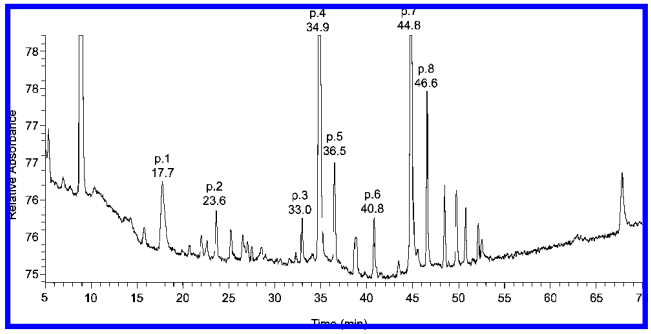

Figure 3. Separation of eight compounds in an extract of the first onion scale determined by LC-MS detected at 280 nm. **Figure 2** gives the names of compounds associated with the eight peaks.

Structural identification of individual compounds in extracts was performed by associating the HPLC peak and the corresponding mass and UV spectra with that of standards, illustrated in **Figures 2**−**4** and **Table 2**. Four unknown peaks were identified as quercetin 3,7,4′-triglucoside (Q3,7,4′G), quercetin 7,4′-diglucoside (Q7,4′G), isorhamnetin 3,4′-diglucoside (IR3,4′G), and isorhamnetin 4′-glucoside (IR4′G) using mass spectral data (**Table 2**). Q3,7,4′G, Q7,4′G, and IR3,4′G were integrated as Q3,4′G equivalents. IR4′G was integrated as Q3G equivalents. Another unknown peak (UIS) was identified as a nonflavonoid (see next section). Because the HPLC retention time of isorhamnetin 3-glucoside (IR3G) in onion extracts coincided with that of the standard but its mass spectrum did not, we did not include data for this flavonoid.

Structure of UIS. UV−visible spectra of flavonoids have two major absorption maxima, band I in the 352−385 nm region associated with the cinnamoyl B-ring of the flavonol molecule and band II in the 205−260 nm region associated with the absorption of the benzoyl A-ring (*14*). By contrast, the UIS spectrum has a maximum absorption at ∼272 nm with a shoulder at 252 nm and several very small peaks at longer wavelengths (**Figure 4**). The spectrum of UIS differs significantly from the illustrated spectra of the seven flavonoids present in the same extract.

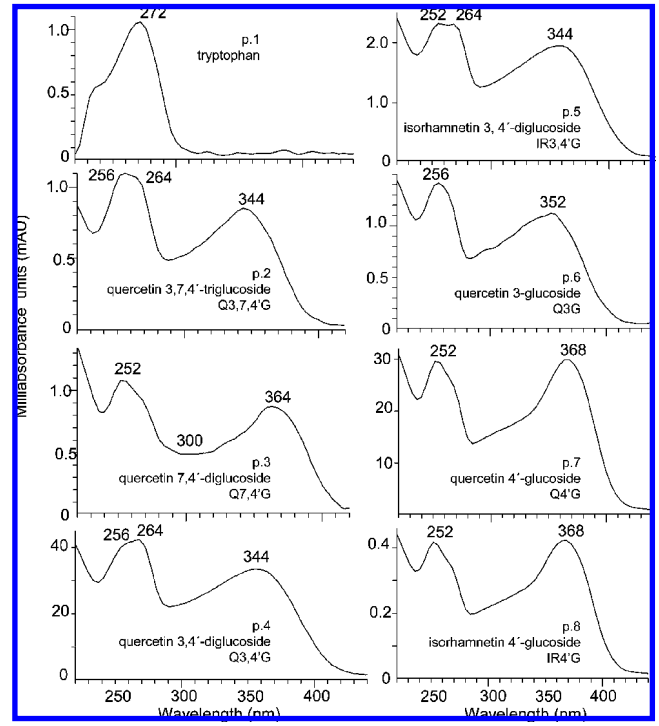

Figure 4. UV−visible spectra of individual peaks isolated from the extract of the first onion scale determined with LC-MS (DAD).

The electrospray ionization (ESI) mass spectrum gave an ion at *m/z* 205.0972 corresponding to the molecular formula of $C_{11}H_{13}N_2O_2$. Eight ^{13}C NMR signals of 11 carbons were observed in the aromatic region, and a carboxyl carbon correlated with the ^1H signals at 3.98 ppm (dd, J = 8.0, 4.9 Hz), 3.39 ppm (dd, J = 15.4, 4.9 Hz), and 3.21 ppm (dd, J = 15.3, 8.0 Hz) in the heteronuclear single-quantum coherence (HSQC) spectrum. The ^1H and ^{13}C NMR chemical shifts were identical to those observed with authentic tryptophan.

Flavonoid Content of Onions and Onion Products. *Onion Bulbs.* **Table 3** shows the following ranges of levels of flavonoids in four commercial Korean onion varieties (in mg/kg): Q3,7,4′G, 0.9−1.3; Q7,4′G, 0.5−1.5; Q3,4′G, 33.3−97.5; IR3,4′G, 1.4−5.8; Q3G, 0.2−0.7; Q4′G, 9.8−17.2; IR4′G, 4.1−13.3. For the Tubo variety, **Table 3** also lists values for small, medium, and large size onions. The total flavonoid content per kilogram of the small-sized onions is 2.1-fold greater than the value for the medium-sized and 2.7-fold greater than the value for the large-sized onions. The small-sized onions had much higher amounts of flavonoids per gram.

Onion Scales. **Table 4** shows the following ranges of individual flavonoids (in mg/kg) in the different scales: Q3,7,4′G, 0.7−3.5; Q7,4′G, 0.1−3.2; Q3,4G′, 26.0−265; IR3,4′G, 2.2−18.0; Q3G, 0.3−2.8; Q4′G, 2.4−101; IR4′G, 1.4−52.1; sum, 221 (fourth) to 530 (first). There was an observed 2.4-fold variation from the highest to lowest value in the sums of the flavonoids and a graduated decrease in the distribution of the flavonoids across the onion bulb from first to seventh scale. We do not know whether the observed variation in the flavonoid content in the onion scales is a general phenomenon for all onion varieties, nor do we know whether the variation will be reflected in the corresponding health-promoting potential of the different scales.

The following are related studies on the flavonoid content of onions that are relevant to the theme of the present study. Onion

Table 2. Retention Times and Mass Spectra of Onion Flavonoids Identified by LC-MS

flavonoid	LC-MS retention time, min	MS spectra $[M - H]^-$, *m/z* (% relative intensity)		
		MS	MS/MS	MS^3
quercetin 3,7,4′-triglucoside	23.6	787.6 (20.5), 786.9 (100), 624.9 (37.2), 545.6 (10.5), 463.5 (14.2)	625.0 (100), 463.1 (16.4)	504.9 (13.2), 463.0 (100)
quercetin 7,4′-diglucoside	33.0	626.2 (33.4), 625.1 (100), 463.0 (73.4)	465.1 (100), 462.9 (66.6), 301.2 (21.5)	302.1 (73.2), 301.0 (100)
quercetin 3,4′-diglucoside	34.9	787.0 (11.1), 627.0 (11.4), 626.0 (26.7), 625.0(100)	463.1 (100)	301.2 (100)
isorhamnetin 3,4′-diglucoside	36.5	640.2 (16.6), 639.2 (100)	476.0 (45.2), 315.0 (100), 313.0 (21.8)	300.1 (100)
quercetin 3-glucoside	40.8	985.4 (23.6), 842.4 (34.7), 741.7 (24.2), 672.8 (24.1), 640.2 (25.5), 562.1 (26.6), 474.5 (14.3), 463.1 (100), 438.0 (23.8), 382.8 (18.4), 300.1 (17.9), 232.7 (15.8)	301.0 (100), 255.1 (23.8)	271.2 (100), 255.3 (46.0), 151.2 (57.6)
quercetin 4′-glucoside	44.8	464.1 (16.7), 463.0 (100), 301.1 (46.1)	301.0 (100)	179.0 (100), 151.0 (37.0)
isorhamnetin 4′-glucoside	46.6	887.4 (26.3), 478.1 (11.6), 477.2 (100)	316.2 (36.1), 315.1 (100)	313.2 (27.4), 300.0 (100), 151.0 (27.4)

Table 3. Flavonoid Content of Korean Onions[d]

onion variety	Q3,74′G	Q7,4′G	Q3,4′G	IR3,4′G	Q3G	Q4′G	IR4′G	sum
Tubo, small size[a]	1.2 ± 0.3	1.5 ± 0.7	97.5 ± 2.9	5.8 ± 1.4	0.4 ± 0.1	17.2 ± 3.0	13.3 ± 1.9	137
Tubo, medium size[b]	0.9 ± 0.1	0.7 ± 0.0	46.1 ± 1.3	1.8 ± 0.4	0.2 ± 0.0	11.2 ± 0.4	4.3 ± 0.2	65
Tubo, large size[c]	0.9 ± 0.1	0.5 ± 0.0	33.3 ± 0.2	1.7 ± 0.1	0.3 ± 0.0	9.8 ± 0.3	5.0 ± 0.3	52
Kaenonboll	1.2 ± 0.1	1.2 ± 0.1	65.3 ± 5.4	2.5 ± 0.4	0.3 ± 0.1	14.3 ± 0.7	5.8 ± 0.2	91
OP	1.1 ± 0.2	1.2 ± 0.1	43.4 ± 0.3	2.2 ± 0.0	0.3 ± 0.0	11.6 ± 0.2	4.9 ± 0.1	65
Red snack	1.3 ± 0.1	1.2 ± 0.2	47.3 ± 0.3	1.4 ± 0.1	0.7 ± 0.1	11.7 ± 0.4	4.1 ± 0.1	68

[a] Listed values are average (mg/kg of fresh weight) ± SD ($n = 3$). Q3,7,4′G, Q7,4′G, and IR3,4′G are expressed as Q3,4′G content; IR4′G is expressed as Q3G content. Abbreviations: Q3,7,4′G, quercetin 3,7,4′-glucoside; Q7,4′G, quercetin 7,4-glucoside; Q3,4′G, quercetin 3,4′-glucoside; IR3,4′G, isorhamnetin 3,4′-glucoside; Q3G, quercetin 3-glucoside; Q4′G, quercetin 4′-glucoside; IR4′G, isorhamnetin 4′-glucoside. [b] Small, 123 ± 3 g. [c] Medium, 223 ± 2 g. [d] Large, 319 ± 2 g.

Table 4. Distribution of Flavonoids in Seven Scales of a Korean Onion Bulb[a]

scale	Q3,74′G	Q7,4′G	Q3,4′G	IR3,4′G	Q3G	Q4′G	IR4′G	sum
1	3.4 ± 0.4 (0.8)	3.2 ± 0.2 (0.7)	265 ± 2.3 (59.4)	18.0 ± 0.2 (4.0)	2.8 ± 1.0 (0.6)	101 ± 3.6 (22.6)	52.1 ± 4.7 (11.7)	446
2	1.8 ± 0.0 (1.1)	1.3 ± 0.0 (0.8)	112.5 ± 3.2 (67.0)	6.7 ± 0.6 (4.0)	0.7 ± 0.1 (0.4)	34.2 ± 1.6 (20.4)	10.5 ± 1.7 (6.3)	168
3	2.0 ± 0.1 (1.3)	1.3 ± 0.1 (0.8)	109.7 ± 2.8 (69.4)	5.5 ± 0.7 (3.5)	0.5 ± 0.0 (0.3)	30.8 ± 2.5 (19.5)	8.2 ± 0.4 (5.2)	158
4	2.3 ± 0.1 (1.7)	1.2 ± 0.1 (0.9)	97.5 ± 5.0 (73.3)	5.1 ± 0.3 (3.8)	0.4 ± 0.0 (0.2)3	21.3 ± 1.7 (16.0)	4.8 ± 0.4 (3.6)	133
5	3.5 ± 0.2 (2.5)	1.4 ± 0.2 (1.0)	125.4 ± 7.2 (88.3)	4.9 ± 0.3 (3.5)	0.5 ± 0.1 (0.4)	2.4 ± 0.3 (1.7)	3.5 ± 0.2 (2.5)	142
6	1.8 ± 0.4 (2.5)	0.7 ± 0.1 (1.0)	56.5 ± 0.1 (79.6)	2.8 ± 0.1 (3.9)	0.3 ± 0.1 (0.4)	7.8 ± 0.0 (11.0)	1.4 ± 0.2 (2.0)	71
7	0.7 ± 0.1 (1.9)	0.1 ± 0.0 (0.3)	26.0 ± 2.9 (72.2)	2.2 ± 0.2 (6.1)	0.3 ± 0.3 (0.8)	4.8 ± 0.8 (13.3)	1.8 ± 0.4 (5.0)	36

[a] See footnote *a* in **Table 3**. Values in parentheses are percent contribution of the individual flavonoid to the sum (total).

bulbs contain wide-ranging amounts of flavonoids, with levels in the following order: red > yellow > white (*3, 15*). Quercetin 4′-glucoside and quercetin 3,4′-diglucoside (Q4′G and Q3,4′G) are prevalent in onions of the 25 characterized flavonols. Flavonoid levels also vary greatly among varieties and growing styles of onions. For example, amounts in Italian onions ranged between 7 for white onions and 600−700 for yellow and red onions, to over 1000 mg/kg of fresh wt for prompt consumption onions such as green onions (*16*). Levels of Q3,4′G and Q4′G in six Australian onion varieties determined by capillary zone electrophoresis and HPLC ranged from <1 to 383 mg/100 g of dry wt quercetin equivalents (*17*). Total flavonoid content (in mg/kg of fresh wt) of five American onion varieties ranged from 285.5 to 580.9, with Q4′G and Q3,4′G contributing about 85−90% of the total (*18*). Levels can also vary significantly in closely related varieties. Trammell and Peterson (*15*) found total quercetin levels of 192−1665 mg/kg in inbred yellow onions. Pungent onion cultivars had higher amounts of flavonoids than did sweet cultivars (*19*).

Growing and harvest conditions can also affect flavonoid content. Swedish researchers found that the quercetin glucoside content of yellow onions (a) correlated with annual variations in global radiation measured in the month of August, (b) increased significantly during postharvest field curing of the onions under sunlight, and (c) was not significantly affected during storage for up to 5 months or by onion size. Q4′G was found to be the prevalent flavonoid and increase the most during field-curing of onions (*20*). Storage of up to 6 months did not affect flavonoid levels of onions grown in the United Kingdom (*21*).

Distribution of flavonoids in the bulb is not uniform. For example, levels of total phenolic compounds of three scales of red, violet, and white onions produced in India ranged in the following order: inner scale < middle scale < outer scale (*22*). This is likely in response to or protection against environmental factors.

Home-Processed Onion Scales. **Table 5** summarizes results from a series of experiments on the influence of seven home-processing conditions we previously used with potatoes (*23*) on the content of flavonoids in the second scale of Tubo white onions. On a percentage basis, loss of total flavonoids ranged as follows: frying, 32.8; sautéing, 20.6; boiling in water with 3% salt, 20; boiling in water with 1% salt, 13.7; steaming, 5.7; microwaving, 4.4; and baking, a gain of 1.1. These results show that with the exception of frying, widely used culinary practices do not significantly affect the flavonoid content of the onion scales.

Previous studies showed that processing can alter the flavonoid content of onions (*1−3, 18*). Roasting of free quercetin glucosides and of onions at 180 °C induced both degradation and transformation of the quercetins to other compounds (*24*). Flavonoid content of Japanese onions decreased from the outer to inner scales as well during boiling of the onions due to release

Table 5. Effect of Home Processing on Flavonoid Content of the Second Scale of Korean Onions

method	treatment	Q3,7,4′G	Q7,4′G	Q3,4′G	IR3,4′G	Q3G	Q4′G	IR4′G	sum
baking	C	2.1 ± 0.1	2.1 ± 0.1	119.1 ± 2.9	3.2 ± 0.1	1.7 ± 0.1	45.1 ± 0.3	14.1 ± 0.8	187
	T	2.4 ± 0.7	2.8 ± 0.0	123 ± 3.0	3.1 ± 0.1	1.9 ± 0.0	39.0 ± 0.3	13.2 ± 0.7	186
	%	(114.3)	(133.3)	(103.4)	(96.9)	(111.8)	(86.5)	(93.6)	(99.5)
boiling (1% salt)	C	2.4 ± 0.0	2.6 ± 0.0	110 ± 1.1	3.8 ± 0.1	1.8 ± 0.0	50.9 ± 1.0	13.0 ± 0.1	185
	T	2.1 ± 0.0	2.2 ± 0.1	101 ± 2.3	3.3 ± 0.0	1.6 ± 0.0	38.0 ± 0.8	11.3 ± 0.3	159
	%	(87.5)	(84.6)	(91.6)	(86.8)	(88.9)	(55.7)	(86.9)	85.9
boiling (3% salt)	C	2.4 ± 0.1	2.2 ± 0.1	118 ± 1.6	3.2 ± 0.0	1.6 ± 0.1	48.8 ± 1.4	10.0 ± 0.3	186
	T	2.0 ± 0.1	1.9 ± 0.1	100 ± 1.0	2.8 ± 0.1	1.1 ± 0.0	30.9 ± 0.5	8.6 ± 0.5	148
	%	(83.3)	(86.4)	(84.8)	(87.5)	(68.8)	(63.3)	(86.0)	79.6
frying	C	2.8 ± 0.0	3.0 ± 0.1	113 ± 1.1	2.5 ± 0.0	2.0 ± 0.1	59.4 ± 0.2	10.6 ± 0.2	193
	T	3.1 ± 0.0	3.1 ± 0.0	74.1 ± 2.5	1.2 ± 0.1	0.9 ± 0.0	34.2 ± 0.5	8.9 ± 0.8	126
	%	(110.7)	(103.3)	(65.5)	(48.0)	(45.0)	(57.6)	(84.0)	65.3
microwaving	C	3.8 ± 0.2	3.6 ± 0.5	118 ± 1.5	3.1 ± 0.1	1.5 ± 0.1	56.4 ± 0.8	9.6 ± 0.3	196
	T	3.2 ± 0.2	3.3 ± 0.1	107 ± 1.4	2.9 ± 0.0	1.2 ± 0.1	51.9 ± 0.8	9.3 ± 0.0	179
	%	(84.2)	(91.7)	(90.8)	(93.5)	(80.0)	(92.0)	(96.9)	91.3
sautéing	C	2.6 ± 0.4	2.2 ± 0.0	120 ± 2.4	2.9 ± 0.5	0.6 ± 0.0	51.0 ± 1.6	11.8 ± 1.4	191
	T	2.6 ± 0.8	2.8 ± 0.8	95.2 ± 4.8	1.9 ± 0.2	0.2 ± 0.0	42.7 ± 5.6	10.2 ± 0.7	156
	%	(100)	(127.3)	(79.6)	(65.5)	(33.3)	(83.7)	(86.5)	81.7
steaming	C	3.8 ± 0.7	2.9 ± 0.7	124 ± 2.4	2.6 ± 0.2	1.2 ± 0.9	47.3 ± 3.0	7.3 ± 1.1	189
	T	2.8 ± 0.6	2.8 ± 0.3	116 ± 4.1	2.4 ± 0.8	0.8 ± 0.5	46.5 ± 3.0	6.1 ± 0.1	177
	%	(73.7)	(96.6)	(93.0)	(92.3)	(66.7)	(98.3)	(83.6)	93.7

[a] See footnote *a* in **Table 3**; C, control; T, treated; values in parentheses are percent C after treatment.

Table 6. Flavonoid Content of the Second and Fourth Onion Scales Irradiated with White Fluorescent Light

scale[a]	time (h)	treatment	Q3,74′G	Q7,4′G	Q3,4′G	IR3,4′G	Q3G	Q4′G	IR4′G	sum
2nd	24	dark	0.8 ± 0.1	2.9 ± 0.3	107 ± 1.1	6.1 ± 0.9	5.5 ± 1.0	43.5 ± 1.4	15.4 ± 0.5	181
	24	light	0.8 ± 0.1	3.9 ± 0.7	126 ± 1.8	7.3 ± 1.2	8.4 ± 1.7	51.5 ± 2.0	25.5 ± 1.4	223
	72	dark	1.5 ± 0.0	4.8 ± 1.4	152 ± 1.8	6.9 ± 1.3	12.4 ± 2.2	104 ± 0.2.6	32.3 ± 0.6	314
	72	light	1.5 ± 0.1	9.7 ± 2.1	186 ± 1.0	9.1 ± 1.0	29.3 ± 5.9	165 ± 3.1	44.2 ± 0.7	445
4th	24	dark	1.0 ± 0.3	2.8 ± 1.3	133 ± 6.9	5.4 ± 1.0	11.3 ± 3.4	52.1 ± 3.0	18.9 ± 6.3	225
	24	light	1.0 ± 0.1	7.7 ± 2.4	141 ± 1.9	6.4 ± 2.2	26.6 ± 8.1	76.0 ± 4.7	26.8 ± 7.4	286
	72	dark	2.0 ± 0.1	4.0 ± 1.0	159 ± 4.2	6.8 ± 2.1	25.7 ± 2.1	96.9 ± 6.0	27.8 ± 5.3	322
	72	light	2.0 ± 0.2	15.8 ± 2.9	229 ± 6.4	15.6 ± 3.6	63.2 ± 9.6	157 ± 4.1	52.1 ± 2.6	535

[a] One set of the second and fourth scales of an onion bulb were stored in the dark, and the second was irradiated with 3000 lx of fluorescent light at 25 °C for 24 and 72 h, respectively. See footnote *a* in **Table 3** for abbreviations.

Table 7. Flavonoid Content of Dehydrated Commercial Onion Products[a]

sample	Q3,7,4′G	Q7,4′G	Q3,4′G	IR3,4′G	Q3G	Q4′G	IR4′G	sum
A	nd	nd	nd	nd	nd	nd	nd	0
B	nd	nd	6.0 ± 0.4 (100)	nd	nd	tr	nd	6.0
C	nd	nd	6.5 ± 0.2 (100)	nd	nd	tr	nd	6.5
D	nd	nd	4.3 ± 0.0 (100)	nd	nd	tr	nd	4.3
E	nd	nd	10.7 ± 0.1 (100)	nd	nd	tr	nd	10.7
F	nd	nd	tr	nd	nd	tr	nd	0
G	nd	nd	tr	nd	nd	tr	nd	0
H	nd	nd	nd	nd	nd	nd	nd	0
I	nd	nd	nd	nd	nd	nd	nd	0
J	nd	nd	nd	nd	nd	nd	nd	0
K	nd	nd	4.3 ± 1.5(69.4)	nd	nd	1.9 ± 0.1 (30.6)	nd	6.2
L	nd	nd	37.3 ± 1.1 (57.7)	tr	nd	27.4 ± 3.9 (42.3)	tr	64.7
M	nd	tr	10.4 ± 0.5 (100)	nd	nd	nd	nd	10.4
N	nd	nd	nd	nd	nd	nd	nd	0
O	12.5 ± 0.4 (3.8)	nd	231 ± 1.5 (69.2)	7.1 ± 0.3 (2.1)	8.4 ± 0.2 (2.5)	63.0 ± 0.7 (18.9)	11.7 ± 0.2 (3.5)	333.7
P	nd	nd	nd	nd	nd	nd	nd	0

[a] Same as footnote *a* in **Table 3**.

into the cooking water and formation of oxidation products (*1*). Lactic acid fermentation altered the flavonoid content of onions (*25*).

Onion Scales Exposed to Fluorescent Light. To extend our knowledge about possible effects of light on the flavonoid content of vegetables (*26*), two sets of the second and fourth scales of the Mansang variety were stored in the dark at 25 °C for 24 and 72 h, respectively. A second set was exposed to fluorescent light (3000 lx) for two photoperiods (24 and 72 h). **Table 6** shows a time-dependent increase in all

flavonoids resulting from exposure to light. The following are calculated increases for the 72 h period (in percent; second, fourth scales): Q7,4′G, 102, 295; Q3,4′G, 23, 44; IR3,4′G, 32, 129; Q3G, 136; 146; Q4′G, 58, 62; IR4′G, 37, 87; sum, 40, 66. The corresponding increases were lower for the 24 h exposure.

The cited data show that (a) the fourth scale is more susceptible to light-induced increases in flavonoid content than the second scale and (b) the percent increase for the different flavonoids in both scales also varies widely. Because onion tissues perceive light as a stress signal, the light-induced biosynthesis of onion flavonoids may to be due to enhanced synthesis of phenylalanine ammonia-lyase and chalcone synthases, enzymes that catalyze the biosynthesis of flavonoids and other phenolic compounds (*27, 28*). A previous study found that UV-B light induced a near doubling of quercetins in onion slices (*26*). Light is known to induce the synthesis of other secondary metabolites such as potato glycoalkaloids (*29*) and the isomerization of piperines (*30*).

Commercial Onion Products. **Table 7** shows results of the analysis of commercial dehydrated onion products listed in **Table 1**. The data show that (a) 8 of the 16 products (A, F, G, H, I, J, N, and P) contained no measurable amounts of flavonoids; (b) 8 products (B, C, D, E, K, L, M, and O) contained Q3,4′G in amounts ranging from 4.3 (D) to 231 (O); three products (K, L, and O) also contained Q4′G in amounts ranging from 1.9 to 63.0; and (c) granulated onion, organic (O), contained 7 substances, all of the flavonoids measured except Q7,4′G, in much higher amounts than in the other products.

The absence or very low levels of flavonoids observed with most of the products was an unexpected finding. It is probably not due to problems with the extraction/analysis because product O contained seven of the eight substances. This onion product was freeze-dried (personal communication, Spice Hunter, Inc., San Luis Obispo, CA). Freeze-drying is a gentler process than other commercial drying processes that use heat. This might account for the difference in flavonoid content compared to similar products.

In summary, we measured the amounts of seven flavonoids in onion bulbs, in seven scales of an onion bulb, in scales subjected to "cooking" methods used in the home, in scales exposed to fluorescent light, and in dehydrated commercial onion products. Free tryptophan was coextracted with the flavonoids. Because its absorbance maximum is at 272 nm, similar to the absorbance maximum of the flavonoids, it appeared in chromatograms measured at 280 nm (**Figures 2** and **4**). Other than tryptophan, our UV chromatograms were relatively free of interference.

We do not know the reasons for the large differences in susceptibilities among individual flavonoids to light-induced synthesis. Because onions are often stored under fluorescent light, possible dietary consequences of the light-induced increases in the flavonoid content merit further study. The results of the flavonoid analyses of commercial dehydrated products are of interest. Because onions are such a good dietary source of flavonoids, using commercial processes that preserve flavonoid content may add value to these products. The present study complements and extends related studies on onion flavonoids and may help consumers select processing methods that minimize loss of flavonoids.

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