AGRICULTURAL AND FOOD CHEMISTRY

Structural Carbohydrate Differences and Potential Source of Dietary Fiber of Onion (*Allium cepa* L.) Tissues

Laura Jaime, Esperanza Mollá,* Almudena Fernández, María A. Martín-Cabrejas, Francisco J. López-Andréu, and Rosa M. Esteban

Departamento de Química Agrícola, Facultad de Ciencias, Universidad Autónoma de Madrid (UAM), 28049 Madrid, Spain

Onion tissues of three varieties were evaluated for dietary fiber (DF) composition. Insoluble (IDF) and soluble (SDF) dietary fibers were subjected to acid hydrolysis, and the resultant neutral sugars, uronic acids, and Klason lignin were quantified. Brown skin exhibited the highest total dietary fiber (TDF) content (65.8%) on a dry matter basis, followed by top (48.5%) and bottom (38.6%), IDF being the main fraction found. The SDF:IDF ratio decreased from inner to outer tissues. Brown skin and outer leaves byproducts appear to be the most suitable sources of DF that might be used in food product supplementation. The chemical composition reveals that cellulose and pectic polysaccharides were the main components of onion DF in all tissues, although differences between them were noticed. An increase in the uronic acids/neutral sugars ratio from inner to outer tissues was found, suggesting that the galactan side chain shows a DF solubilization role.

KEYWORDS: Onion (Allium cepa L.); dietary fiber; structural carbohydrates; tissues; byproducts

INTRODUCTION

Onion (*Allium cepa* L.), a widespread Alliaceae plant, is one of the main vegetables consumed in Europe either raw or processed in different ways. The bulb or edible part is formed by the swollen leaf bases (1, 2). Onion bulbs are known to exhibit heart stimulative, diuretic, expectorant, and antibacterial properties. They also stimulate gastrointestinal transit, promote bile production, and reduce sugar and lipid levels (3).

The onion-processing industry produces annually >450000 tonnes of onion waste in the European Union. These residues come mainly from the recent market demand of peeled onions (e.g., onion rings). The major industrial peeling byproducts are the outer two fleshy leaves and lesser quatities of onion brown skin and tops and bottoms of bulbs. Nowadays, food industries are forced by environmental regulations to develop productions without secondary residues. Due to their strong aroma, these onion wastes are not suitable to be used as fodder, nor can they be left above the land as an organic fertilizer because of the rapid development of phytopathogenic agents such as Sclerotium cepivorum (white rot) (4). Likewise, as a result of their high percentage of moisture, their removal by combustion becomes rather expensive. These disadvantages are why onion producers and processor industries have suggested the conversion of onion wastes into food ingredients such as flavor components, dietary fiber, or fructans products.

* Corresponding author (telephone 34-91-3975258; fax 34-91-3973830; e-mail esperanza.molla@uam.es).

Recently, several studies on flavor constituents (5, 6) and phenolic compounds (7, 8) in onion bulbs have been carried out; moreover, brown outer skin has attracted attention as a good source of pigments and gelling pectins (9, 10).

Many authors have studied the dietary fiber (DF) content in peeled onions (11-13). Onios, like other vegetables, showed high levels of moisture with less quantities of dietary fiber. Nevertheless, onion DF showed a better soluble/insoluble dietary fiber (SDF:IDF) ratio than other vegetables that will be connected with differents metabolic and physiological effects. Similar experiments have been carried out on plant cell walls, and their polysaccharide composition is formed by cellulose, galactan-rich pectins, and xyloglucans (9, 14-16). However, very little information is available concerning the DF constituents of different onion cultivars and their respective tissues.

The objective of the present study was to provide precise information on the chemical composition of onion tissues and varieties, with special attention to dietary fiber. Such information may be useful to food technologists for the real-potential exploitation of onion byproducts as source of dietary fiber.

MATERIALS AND METHODS

Three varieties of mature onions (*Allium cepa* L. cv. Sturon, Hysam, and Grano de Oro) were provided from onion producers (British Onion Producers Association). Ten onion bulbs were taken randomly to form 10-bulb samples for each variety in triplicate and processed as follows: (1) top and (2) bottom (\sim 5–10 mm sliced off the top and bottom ends of the onions); (3) brown dry outer skin; (4) outer two fleshy leaves; and (5) remaining inner fleshy leaves. The separated

| Table 1. Ch | iemical F | Parameters | of C |)nion \ | Varieties |
|-------------|-----------|------------|------|---------|-----------|
|-------------|-----------|------------|------|---------|-----------|

| | | variety | skin | top | bottom | outer | inner | whole |
|------------------------------------|-----|--------------|-----------------------------|--|-------------------------------|-------------------------------|--------------------------------------|-------------------------------|
| dry matter ^a (%) | | | *** | *** | *** | *** | *** | *** |
| j | *** | Sturon | $82.9 \pm 6.6a^{a}$ | $21.5 \pm 2.3 \text{ bc}^{b}$ | $26.8 \pm 1.2 h^{a}$ | 14.3 ± 2.3 c ^a | $16.6 \pm 2.7c^{a}$ | $17.0 \pm 2.8c^{a}$ |
| | *** | Hysam | $66.0 \pm 1.7a^{b}$ | 25.7 ± 6.1 ^a | $24.4 \pm 4.6 \mu^{a}$ | $12.4 \pm 1.6 d^{b}$ | $12.8 \pm 0.2 d^{b}$ | $15.1 \pm 2.6c^{b}$ |
| | * | Grano de Oro | $60.3\pm6.8_a{}^c$ | $17.7 \pm 6.7 b^{c}$ | $17.5 \pm 0.9 ^{b}{b}$ | $9.7 \pm 1.2^{c}_{c}$ | $8.8\pm0.5_{\text{cd}}{}^{\text{c}}$ | $10.8 \pm 3.2 c^{c}$ |
| total nitrogen ^a | | | *** | * | *** | NS | *** | *** |
| (g kg ⁻ 1 of DM) | *** | Sturon | $4.9 \pm 0.2 e^{b}$ | $10.7 \pm 0.7 d^{a}$ | $23.5 \pm 1.5a^{b}$ | 15.0 ± 0.7 c ^a | 17.3 ± 0.1 h ^b | $15.9 \pm 1.1 \text{ bc}^{b}$ |
| | *** | Hysam | 5.4 ± 0.3 a | $8.2 \pm 0.1 d^{c}$ | $21.2 \pm 0.1^{c}_{a}$ | 15.4 ± 0.4 c ^a | $16.3 \pm 0.8 { m hc}^{ m C}$ | $17.3 \pm 0.3 b^{2}$ |
| | *** | Grano de Oro | $2.6 \pm 0.2_{e}$ c | 9.7 ± 0.1 d ^b | 35.0 ± 2.3 a ^a | 15.6 ± 0.2 c ^a | $18.1 \pm 0.5 b^{a}$ | $15.8 \pm 1.1 ^{b}_{c}$ |
| ash^a (g kg ⁻¹ of DM) | | | *** | *** | *** | *** | *** | |
| don (ging of bin) | *** | Sturon | $85.0 \pm 2.8 \mu^{a}$ | $71.0 \pm 1.0c^{b}$ | $102.5 \pm 1.5a^{b}$ | 33.1 ± 1.1ď | $32.9 \pm 2.0 d^{b}$ | $34.3 \pm 1.6 d^{c}$ |
| | *** | Hysam | $68.9 \pm 0.7 c^{c}$ | 96.3 ± 1.9 _b ^a | $107.7 \pm 0.6a^{a}$ | $31.7 \pm 1.3 de^{C}$ | $33.1 \pm 2.5 d^{b}$ | $37.5 \pm 0.9 d^{b}$ |
| | *** | Grano de Oro | 71.8 ± 1.7 ^b | $69.9 \pm 0.8_{bc}^{c}$ | $96.5 \pm 1.9^{a^{c}}$ | $53.5 \pm 2.3_{de}^{a}$ | $57.0 \pm 2.3 d^{a}$ | $55.1 \pm 2.0_{de}^{a}$ |

^a Mean \pm SD (n = 9). Mean values of each column followed by a different superscript letter significantly differ when subjected to DMRT (P < 0.05). Mean values of each row followed by a different subscript letter in bold significantly differ when subjected to DMRT (P < 0.05). Asterisks in each column indicate statistical differences between varieties: ***, P < 0.001; *, P < 0.05; NS, not statistical differences. Asterisks in each row indicate statistical differences between tissues: ***, P < 0.001; *, P < 0.05; NS, not statistical differences. Asterisks in each row indicate statistical differences between tissues: ***, P < 0.001; *, P < 0.05; NS, not statistical differences.

tissues were immediately frozen in liquid nitrogen after cutting, freezedried, sieved (0.5 mm), and stored at -20 °C until analyzed.

Fresh weights of whole onions and their different tissues were determined in 100 onion bulbs using a balance $(\pm 0.01 \text{ g})$ (17), whereas height and diameter were determined in 10 randomized bulbs of each variety (18). The fresh weight, diameter, and height of the whole onions varied from Grano de Oro to Hysam, the former showing the biggest onion bulbs.

Dry Matter Determination. Fresh tissues were weighed in triplicate $(\pm 0.1 \text{ mg})$ from each 10-bulb sample and dried at 65 \pm 1 °C in a vacuum oven to constant weight. Moisture content was obtained by difference between fresh and dried weight of the different tissues. Tissues with a higher content of water needed longer dry times (19).

Total Nitrogen Determination. Total nitrogen content was determined in triplicate from each 10-bulb sample by using the Kjeldahl procedure (20).

Ash Content Determination. Ash content was determined in triplicate from each 10-bulb sample by calcination of samples using a muffle furnace at 525 °C for 5 h (20).

Dietary Fiber Determination. Mes-Tris AOAC Method 991.43 was used for DF determination (20). Two replicates of each 10-bulb sample were taken to complete the six-sample analysis method. The principle of the method was based on the use of three enzymes (heat-stable α -amylase, protease, and amyloglucosidase) under different incubation conditions to remove starch and protein contents. DF fractions were obtained as indigestible residues after enzymatic digestion of nondietary fiber components; the insoluble residues were isolated by filtration, and soluble fiber was precipitated with ethanol. Dried residues corresponded to insoluble dietary fiber (IDF) and soluble dietary fiber (SDF), respectively. Determination of residual ashes and proteins (as Kjeldahl \times 6.25) was carried out in the residues for corresponding corrections. Total dietary fiber (TDF) was calculated as the sum of IDF and SDF. Kjeldahl nitrogen and ash contents were assayed according to standard procedures (20).

Chemical Analysis of Dietary Fiber Components. The composition of DF was determined after acid hydrolysis of fiber residues obtained according to AOAC modified Method 991.43 (*20*); the soluble fraction was obtained by dialysis for 48 h at 4 °C against distilled water.

Insoluble fiber residues $(100.0 \pm 0.1 \text{ mg})$ were subjected to 12 M H₂SO₄ treatment for 3 h at room temperature, followed by dilution to 0.6 M H₂SO₄ hydrolysis at 100 °C for 3 h and also to 0.6 M H₂SO₄ hydrolysis at 100 °C for 3 h. Soluble fiber residues $(100.0 \pm 0.1 \text{ mg})$ were hydrolyzed only with 0.6 M H₂SO₄ at 100 °C for 3 h (21). The acid hydrolysis released the different fiber components, neutral sugars, and uronic acids. The insoluble residue after 12 + 0.6 M H₂SO₄ hydrolyses was recovered quantitatively over a glass filter (Pyrex No. 4), washed thoroughly with pure water, and dried for 18 h at 105 °C, corresponding to Klason lignin residue.

The hydrolysates were neutralized using AG4-X4 resin (Bio-Rad Laboratories, Richmond, CA). The neutral sugar composition of the

hydrolysates was determined by HPLC using a microguard column (Aminex Carbo-P, Bio-Rad) in series with a carbohydrate analysis column (Aminex HPX-87P heavy metal, 300 mm \times 7.8 mm, Bio-Rad) operated at a flow rate of 0.5 mL/min using a refractive index detector. Galactose and rhamnose coelute from this column. The amounts of sugars present were computed using the System Gold 7.0 version software after calibration with standard sugars (Sigma, St. Louis, MO). Erythritol (Sigma), added just before neutralization, was used as the internal standard. Recoveries from the hydrolytic procedure were determined by subjecting standard sugars to the total analytical procedure (22).

Uronic acids were determined colorimetrically by adapting the 3-hydroxydiphenyl method of Blumenkrantz and Asboe-Hansen (23) with D-galacturonic acid (Sigma) (21).

Statistical Analysis. Results were analyzed using Duncan's multiple range test (DMRT) (24). Differences were considered significant at $P \le 0.05$. Linear regression analysis and correlation matrices between variates over all varieties were carried out using StatGraphics Plus, version 3.1. for Windows.

RESULTS AND DISCUSSION

Chemical parameters for the onion varieties are presented in Table 1. With regard to the dry matter (DM) values, no significant differences were observed between inner and outer leaves or between top and bottom. The fleshy tissues (inner and outer leaf tissues) showed the lowest content of DM, whereas brown skin tissues had the highest contents of DM, showing a wide range of values. Therefore, DM content increased from younger (inner tissue) to older leaves (brown skin tissue). Whole onion dry matter was similar to fleshy tissues in all varieties because of the major contribution of these tissues to whole onion weight. In general, the Grano de Oro variety showed the lowest amounts of DM, whereas the Sturon variety presented the highest content.

Bulb DM content is an important quality parameter to the onion dehydration industry because it has a direct impact on the energy required for drying (25). Several other quality attributes, such as pungency (26) and storage life (27) are related to DM content. Sinclair et al. (18) classified 49 onion varieties on the basis of their DM content. Varieties for fresh market showed DM content ranging from 74 to 147 g kg⁻¹, whereas the DM content of dehydrating varieties ranged from 159 to 215 g kg⁻¹. Thus, in agreement with Sinclair et al. (18), Grano de Oro and Hysam onion varieties could be labeled as "fresh market" types, whereas the Sturon variety could be a "dehydrating" type. Likewise, a higher content of DM facilitates better storage and transport (28), and only the Sturon variety showed

 Table 2. Content of Insoluble, Soluble, and Total Dietary Fiber and Its

 Distribution of Onion Varieties (Percent of Dry Matter)

| tissue | IDF ^a | SDF ^a | TDF | SDF:IDF |
|--------------|--------------------------|--------------------------|------|---------|
| Sturon | *** | *** | | |
| skin | 59.3 ± 0.5^{a} | 4.4 ± 0.4^{c} | 63.7 | 1:13 |
| top | 38.2 ± 0.8^{b} | 4.5 ± 0.2^{c} | 42.7 | 1:8 |
| bottom | $26.2 \pm 0.8^{\circ}$ | 8.5 ± 0.4^{a} | 34.7 | 1:3 |
| outer | 9.9 ± 0.4^{d} | $4.6 \pm 0.3^{\circ}$ | 14.5 | 1:2 |
| inner | $5.8\pm0.6^{\mathrm{e}}$ | 3.5 ± 0.1^{b} | 9.3 | 1:2 |
| whole | 9.2 ± 0.6^{d} | 5.7 ± 0.6^{b} | 14.9 | 1:2 |
| Hysam | *** | *** | | |
| skin | 60.8 ± 0.4^{a} | 4.6 ± 0.3^{d} | 65.4 | 1:13 |
| top | 46.1 ± 0.8^{b} | $3.4\pm0.2^{\mathrm{e}}$ | 49.5 | 1:13 |
| bottom | $32.8 \pm 0.5^{\circ}$ | 7.4 ± 0.4^{a} | 40.2 | 1:4 |
| outer | 15.0 ± 0.2^{e} | $5.1 \pm 0.2^{\circ}$ | 20.1 | 1:3 |
| inner | 5.7 ± 0.5^{f} | 5.2 ± 0.2^{c} | 10.9 | 1:1 |
| whole | 18.2 ± 0.8^{d} | 6.7 ± 0.3^{b} | 24.9 | 1:3 |
| Grano de Oro | *** | *** | | |
| skin | 66.6 ± 0.8^{a} | 1.7 ± 0.1^{e} | 68.3 | 1:39 |
| top | 48.7 ± 1.3^{b} | 4.7 ± 0.4^{b} | 53.4 | 1:10 |
| bottom | $30.6 \pm 0.2^{\circ}$ | 10.2 ± 0.3^{a} | 40.8 | 1:3 |
| outer | 24.4 ± 1.2^{e} | 4.2 ± 0.2^{d} | 28.6 | 1:6 |
| inner | 6.9 ± 0.3^{f} | 4.7 ± 0.5^{b} | 11.6 | 1:1.5 |
| whole | 26.6 ± 0.1^{d} | 4.4 ± 0.2^{c} | 31.0 | 1:6 |
| | | | | |

^{*a*} Mean ± SD (n = 6). Mean values of each column followed by a different superscript letter significantly differ when subjected to DMRT (P < 0.05). Asterisks in each column indicate statistical differences between tissues: ***, P < 0.001.

low percentages of sprouting bulbs after 6 months of storage, according to its higher DM content (19).

Remarkable differences were detected in Kjeldahl nitrogen content between onion tissues (Table 1). In general, the onion bottom was the tissue with a higher content of nitrogen. In most of varieties, the outer two fleshy leaves showed a nitrogen content significantly lower than that of the inner part, suggesting that nitrogen distribution tends to increase from outer to inner leaves (younger leaves). Top tissue and especially brown skin showed lower nitrogen contents than fleshy tissues. Slight differences were detected in nitrogen content between onion varieties depending on the tissue studied. It appears, therefore, that the differences between onion tissues may show a translocation of nitrogen compounds from the senescenced leaves (brown skin and top tissues) down to the bulb during the onion ripening. According to this, Nilsson (29), in a study on the chemical composition of onion bulbs, indicated that this translocation increased the content of free amino acids in the bulbs, especially arginine, in contrast to protein nitrogen content that decreased during maturation. Furthermore, the uneven distribution of arginine, with a higher concentration in the bulb center, could suggest that its synthesis would take place in the bulbs.

Ash contents have also provided valuable information (Table 1). Onion bottom was the tissue with the highest content of ashes, probably because this tissue comprised the plant roots, in which the nutrient uptake occurs. In contrast to nitrogen behavior, brown skin and top tissue showed higher ash contents than fleshy tissues. Whole onion showed an ash content similar to that of inner or outer fleshy leaves, probably due to the major contribution of these tissues to the total whole onion weight.

Of nutritional interest was the study of DF fractions due to their important physiological properties. SDF increases the viscosity of the stomach contents, thereby allowing down-mixing and absorption of nutrients, whereas IDF reduces intestinal transit time and increases the bulk of the food mass (*30*). Great differences between the IDF contents of whole onion in the three varieties studied (Table 2) were observed, being 60% higher in Grano de Oro than in the Sturon variety. These results are in agreement with the different levels found in the literature (11-13). The three varieties showed the same trend in IDF content of onion tissues. Brown skin gave the highest content, followed by top and bottom tissues. Because the top and bottom tissues are formed by a mixture of inner, outer, and skin tissues, the higher skin level of the top is reflected in higher amounts of IDF with respect to bottom content. Likewise, the two outer leaves and the whole onion showed very similar contents of IDF. The inner leaves tissue exhibited the lowest IDF values. It is interesting to point out the different values found in outer and inner leaves. Apparently, these tissues seem to show the same physical characteristics; however, in practice, the IDF values obtained gravimetrically are higher in outer leaves than in inner tissue. These results may suggest an increasing trend in DF content from inner to outer fleshy leaves of onion bulbs as a result of a higher cell wall development. It seems that onion and especially certain tissues, such as brown skin and top and bottom tissues, had very high contents of IDF, which is very interesting for their potential industrial use as a fiber source.

In addition, a linear relationship was exhibited between DM and IDF contents of the different tissues in the three varieties studied ($r = 0.8679^{**}$, 0.897^{**} , and 0.844^{**} in Sturon, Hysam, and Grano de Oro varieties, respectively). The *r* values imply that IDF increased as DM increased, and it could be related to the senescence process of bulb fleshy leaves.

Furthermore, a negative correlation was found between IDF and nonstructural carbohydrates contents of the different tissues measured in earlier studies (*31*); these results might suggest a clear influence of bulb physiology because nonstructural carbohydrates increased in inner leaves in contrast to structural carbohydrates (IDF) and according to their different metabolic activities.

The SDF contents were significantly lower than IDF contents (Table 2) in all tissues. The onion varieties showed a higher content of SDF in bottom tissues (7.4-10.2%) followed by whole onion, except for the Grano de Oro variety. In contrast to IDF behavior, SDF levels exhibited no drastic differences between onion tissues.

With regard to TDF contents (Table 2), the same trend as for IDF levels was observed because of the major contribution of this fraction in the global determination of dietary fiber. Therefore, TDF contents showed a positive correlation with DM and a negative correlation with the nonstructural carbohydrates reported in a previous paper (*31*).

Soluble/insoluble fiber ratios are important from both dietary and functional perspectives. To be acceptable, a dietary fiber ingredient must perform in a satisfactory manner as a food ingredient (32). It must be kept in mind that fiber enrichment not only influences the overall quality of food by changing its physiological properties but also significantly affects the sensorial properties of a product. Besides the amount of DF added, the ratio of insoluble and soluble fiber is an important variant related to structural and also sensorial properties (33, 34). It is generally accepted that those fiber sources suitable to be used as a food ingredient should have an SDF:IDF ratio close to 1:2. In this respect, onion fleshy leaves, whole onion, and bottom tissue provided the more suitable onion tissues for food supplementation. With regard to onion tissues, the SDF:IDF ratio decreases from inner to outer tissues, as the IDF levels increase. Therefore, brown skin and top tissues showed a highly insoluble dietary fiber, unsuitable for food supplementation. Nevertheless, brown skin was the tissue with the highest content of DF on a DM basis.

Table 3. Dietary Fiber Yield (Mean of the Three Varieties, Percentage of DF per Onion Bulb)

| | skin | top | bottom | outer | inner |
|-----|------|-----|--------|-------|-------|
| IDF | 44 | 8 | 6 | 20 | 22 |
| SDF | 10 | 3 | 6 | 27 | 54 |
| TDF | 36 | 7 | 6 | 22 | 29 |

The study of DF yield of onion tissues as grams of dietary fiber per onion bulb can be used to know the real contribution of each tissue to dietary fiber of whole onion (Table 3). This comparative study resulted from the fact that onion tissues with high fiber content accounted for a low weight of the whole onion (e.g., brown skin) and vice versa (e.g., inner part). Brown skin and inner part were the major contributors to IDF of onion bulbs followed by the tissues of the outer two fleshy leaves. With regard to SDF, the inner part and outer two fleshy leaves showed more than 50 and 25% of whole onion SDF, respectively. Therefore, brown skin and the two outer leaves constituted the byproducts from onion peeeling that showed the main contents of total dietary fiber of the whole onion. Nervertheless, the different fiber compositions of both tissues are worth mentioning because fiber from brown skin was mainly insoluble fiber, whereas fiber from outer fleshy leaves showed a more balanced composition (SDF:IDF ratio of 1:3). According to this, chemical, biochemical, or physical treatments to modify DF characteristics of onion skin could be a useful tool to improve the SDF:IDF ratio in order to use this onion waste in fiber-enriched products.

The profile of the sugar composition of IDF (Table 4) reveals not varietal differences between the IDF constituents of the onion tissues studied. The bulk of the IDF of whole onion mainly comprised carbohydrates, glucose and uronic acids being the main sugar constituents, followed by galactose, whereas xylose, mannose, and arabinose appeared in minor amounts. The glucose component was mainly cellulosic in origin; <10% was released by 0.6 M H₂SO₄ hydrolysis (22). This fact also confirms the absence of starch. From these results, cellulose and polyuronides were inferred to be the main polysaccharides of IDF. The residues obtained after acid hydrolysis were referred to as Klason lignin; they seemed to be higher than expected. probably due to the presence of cell wall or coprecipitated intracellular protein residues (35). Guijarro (36) confirmed the presence of coprecipitated protein in Klason lignin of onion dietary fiber ($\sim 25\%$).

Although the inner part contributed most to the whole onion weight, the IDF yield and carbohydrate composition of whole onion and inner leaves showed certain differences. The main difference was that the IDF yield of the inner part was significantly lower than the IDF of the whole onion in most varieties. In addition, the level of IDF uronic acids was lower in the inner part, whereas the galactose percentage was slightly higher. As a result, the uronic acid/neutral sugar (galactose + arabinose) (UA:NS) ratio was lower in inner leaves compared to that of the whole onion.

Moreover, the outer (older) two fleshy leaves gave a higher IDF yield when compared to the inner leaves tissue. Other differences between both fleshy tissues were observed in the percentages of glucose and the uronic acid percentage, which were lower and higher, respectively, in outer fleshy leaves compared to inner leaves. As a result, IDF from outer two leaves comprised mainly pectic polysaccharides, whereas the inner part IDF was mainly formed by cellulose.

Top and bottom tissues were formed by a mixture of inner and outer leaves and brown skin as reflected by the chemical composition of their DF. Carbohydrates accounted for 91 and 78% of IDF from top and bottom tissue, respectively. The carbohydrate composition showed the presence of pectic polysaccharides, as inferred from the percentages of uronic acid, galactose, and arabinose, and the presence of cellulose. The levels of xylose and arabinose in bottom tissues were higher than those found in other onion tissues.

Brown skin showed a very high yield of IDF constituted mainly by carbohydrates (95%). The profile of the sugar composition of the skin IDF exhibited lower levels of galactose when compared to the other onion tissues, resulting in the highest UA:NS (galactose + arabinose) ratio. This ratio increased from younger leaves (inner part) to older tissues (brown skin), suggesting that it could be caused by a loss of galactan side chains as a result of galactosidase activity. This loss might increase the cross-linking between pectic polysaccharides and, hence, the packing of pectin strands, which has been related to the firmness development of cells and waterproofing characteristics of the onion skin (4).

It is interesting to point out that arabinose, xylose, and manose did not suffer drastic differences between tissues; nevertheless, galactose contribution increased from older tissues (1% in brown skin) to inner leaves (11% in inner part). Unlike galactose, the

| | | | | carbohydra | tes ^a (%) | | total | Klason | | | |
|--------|---------|-----|-----|------------|----------------------|-----|-------|--------|----------------|-------|-------|
| tissue | variety | Glc | Xyl | Gal/Rha | Ara | Man | UA | sugars | lignin | total | UA:NS |
| skin | Sturon | 46 | 2 | 2 | 1 | 4 | 44 | 388.5 | 42.3 ± 2.3 | 430.8 | 12.1 |
| | Hysam | 37 | 2 | 1 | 1 | 3 | 56 | 549.1 | 15.6 ± 0.9 | 564.7 | 31.8 |
| | Grano | 52 | 2 | 1 | 1 | 3 | 42 | 603.2 | 16.1 ± 3.6 | 619.3 | 33.5 |
| top | Sturon | 54 | 4 | 6 | 2 | 8 | 26 | 269.0 | 41.5 ± 0.7 | 310.5 | 3.3 |
| | Hysam | 43 | 2 | 2 | 1 | 3 | 49 | 354.3 | 30.3 ± 7.7 | 384.6 | 15.7 |
| | Grano | 31 | 1 | 3 | 1 | 1 | 63 | 364.8 | 23.3 ± 3.8 | 388.1 | 20.1 |
| bottom | Sturon | 40 | 5 | 9 | 6 | 9 | 32 | 152.2 | 72.0 ± 11.0 | 224.2 | 2.2 |
| | Hysam | 46 | 4 | 7 | 3 | 2 | 38 | 282.3 | 53.7 ± 0.3 | 336.0 | 4.2 |
| | Grano | 27 | 6 | 6 | 3 | 6 | 52 | 235.2 | 65.4 ± 5.3 | 300.6 | 5.8 |
| outer | Sturon | 46 | 3 | 18 | 4 | 3 | 25 | 78.5 | 6.4 ± 0.7 | 84.9 | 1.2 |
| | Hysam | 39 | 2 | 9 | 1 | 2 | 47 | 149.3 | 8.2 ± 1.0 | 157.5 | 4.7 |
| | Grano | 29 | 2 | 9 | 2 | 4 | 55 | 210.7 | 15.0 ± 2.1 | 225.7 | 5.4 |
| inner | Sturon | 52 | 3 | 15 | 2 | 5 | 22 | 52.1 | 8.2 ± 0.5 | 60.3 | 1.3 |
| | Hysam | 53 | 2 | 9 | 2 | 10 | 24 | 50.6 | 6.4 ± 0.6 | 57.0 | 2.2 |
| | Grano | 57 | 3 | 9 | 2 | 8 | 22 | 63.7 | 8.6 ± 2.0 | 72.3 | 2.1 |
| whole | Sturon | 43 | 4 | 14 | 2 | 6 | 31 | 65.7 | 12.0 ± 0.1 | 77.7 | 1.9 |
| | Hysam | 50 | 2 | 5 | 1 | 2 | 41 | 147.9 | 8.2 ± 1.0 | 156.1 | 7.2 |
| | Grano | 47 | 2 | 8 | 1 | 1 | 40 | 181.2 | 13.1 ± 2.9 | 194.3 | 4.6 |

^a Data are expressed as percentage of total sugars.

 Table 5. Composition of Soluble Dietary Fiber in Onion Varieties (Grams per Kilogram of DM)

| | | | | carbohydra | tes ^a (% | 5) | | total | |
|--------|---------|-----|-----|------------|---------------------|-----|----|--------|-------|
| tissue | variety | Glc | Xyl | Gal/Rha | Ara | Man | UA | sugars | UA:NS |
| skin | Sturon | 13 | 2 | 11 | 3 | 13 | 57 | 20.2 | 3.9 |
| | Hysam | 12 | 1 | 6 | 1 | 10 | 70 | 34.9 | 9.7 |
| | Grano | 14 | 1 | 4 | 1 | 16 | 65 | 22.2 | 14.4 |
| top | Sturon | 10 | 1 | 27 | 2 | 8 | 52 | 37.6 | 1.8 |
| | Hysam | 13 | 1 | 19 | 3 | 14 | 50 | 37.4 | 2.3 |
| | Grano | 13 | 2 | 25 | 3 | 5 | 52 | 34.6 | 1.9 |
| bottom | Sturon | 9 | 0 | 25 | 5 | 6 | 55 | 47.6 | 1.8 |
| | Hysam | 5 | t | 24 | 7 | 10 | 54 | 59.8 | 1.7 |
| | Grano | 5 | 0 | 30 | 8 | 2 | 54 | 60.4 | 1.4 |
| outer | Sturon | 11 | t | 29 | 2 | 14 | 44 | 39.3 | 1.4 |
| | Hysam | 18 | t | 26 | 2 | 13 | 41 | 33.2 | 1.5 |
| | Grano | 7 | t | 28 | 2 | 11 | 53 | 26.8 | 1.8 |
| inner | Sturon | 12 | t | 38 | 2 | 5 | 43 | 41.5 | 1.1 |
| | Hysam | 4 | 1 | 38 | 2 | 14 | 41 | 52.6 | 1.1 |
| | Grano | 7 | t | 44 | 1 | 6 | 42 | 40.3 | 0.9 |
| whole | Sturon | 9 | t | 28 | 2 | 20 | 41 | 46.7 | 1.4 |
| | Hysam | 7 | t | 36 | 2 | 10 | 45 | 46.7 | 1.2 |
| | Grano | 8 | t | 29 | 2 | 10 | 52 | 33.1 | 1.7 |

^a Data expressed as percentaged of total sugars.

uronic acids contribution decreased from older leaves (47% in brown skin) to inner leaves (23% in inner part). This resulted in a lower UA:NS ratio in fresh leaves as compared to brown skin. Therefore, fleshy leaves were formed by highly branched pectic polysaccharides, whereas in brown skin there was a predominance of homogalacturonans due to the action of galactosidases. Despite the fact that cellulose, xyloglucans, and pectic polysaccharides were the main constituents of IDF of all tissues, some differences among them were noticed.

Furthermore, chemical analysis of the IDF fraction of Sturon, Hysam, and Grano de Oro varieties showed that the levels of neutral sugars and uronic acids determined after 12 + 0.6 M acid hydrolyses were higher than those obtained by 0.6 M H₂-SO₄ in all tissues except for galactose and arabinose (data not shown). Therefore, strong acid conditions caused a significant destruction of these sugars. These results might indicate that cellulose microfibrills were closely connected to hemicelluloses (xyloglucans) and pectic polysaccharides different from arabinans and galactans. The arabinan and galactan chains seemed to be dispersed in the cell wall matrix and, thus, they were more accessible to sulfuric acid action. Ha et al. (16) showed in NMR studies of hydrated and dehydrated onion cells that cellulose microfibrills were strongly associated with xyloglucans. Furthermore, they found that the pectic matrix was formed by "hard" calcium pectate gel regions (homogalacturonans) and "soft" arabinan, galacturonan, and galactan regions.

Interestingly, the carbohydrate composition of the SDF fraction of whole onions showed the presence of uronic acid and galactose as the main sugar constituents (Table 5). The sugar profile of SDF from inner tissue and the outer two fleshy leaves showed that uronic acid and galactose accounted for ~80% of total sugars. Lower levels of galactose were found in outer leaves (28%) compared to inner leaves (40%). Arabinose appeared in minor amounts, and only traces of xylose were detected in these tissues. Brown skin exhibited certain differences compared to the previous tissues. As in the IDF fraction, the levels of galactose were the lowest, resulting in the highest UA:NS ratio (8:1).

With regard to neutral sugars, bottom tissues showed the highest percentage of arabinose (7%) as in IDF fraction, whereas xylose was found in minor amounts in older tissues, and it was scarcely detected in fleshy leaves. Moreover, as in the insoluble fraction, the galactose percentage decrease from inner to outer tissues in contrast to uronic acids behavior. These trends brought about an increase in UA:NS ratio from inner to outer tissues, indicating that higher amounts of rhamnogalacturonans substituted with galactans were found in fleshy leaves. The results are in agreement with those of Ng et al. (4).

Therefore, significant differences were detected in the carbohydrate composition of TDF from different tissues (Table 6). The levels of xylose in bottom tissues were higher compared to other onion tissues, suggesting the major presence of xyloglucans in that tissue, decreasing its content in the other tissues. According to IDF and SDF trends, the TDF of inner tissues contained galactose-rich pectic polysaccharides. Outer leaves had progressively less pectic galactose, and the brown skin contained minor amounts of galactose. Thus, an increasing trend in the UA:NS ratio from the inner to the outer tissues was observed, suggesting that galactan and arabinan side chains were gradually lost from inner to outer tissues as cell wall soluble components decreased.

Table 6. Composition of Total Dietary Fiber in Onion Varieties (Grams per Kilogram of DM)

| | | | | carbohydra | total | total sugars + | | | | |
|--------|---------|-----|-----|------------|-------|----------------|----|--------|---------------|-------|
| tissue | variety | Glc | Xyl | Gal/Rha | Ara | Man | UA | sugars | Klason lignin | UA:NS |
| skin | Sturon | 44 | 2 | 3 | 1 | 5 | 45 | 408.7 | 451.0 | 10.7 |
| | Hysam | 36 | 2 | 1 | 1 | 3 | 57 | 584.0 | 599.6 | 27.3 |
| | Grano | 51 | 2 | 1 | 1 | 3 | 42 | 625.4 | 641.5 | 31.2 |
| top | Sturon | 48 | 4 | 9 | 2 | 8 | 29 | 306.6 | 348.1 | 2.8 |
| | Hysam | 40 | 2 | 4 | 1 | 4 | 49 | 391.7 | 422.0 | 9.9 |
| | Grano | 29 | 1 | 5 | 1 | 2 | 62 | 399.4 | 422.7 | 11.8 |
| bottom | Sturon | 33 | 4 | 13 | 6 | 8 | 37 | 199.8 | 271.8 | 2.0 |
| | Hysam | 39 | 4 | 10 | 3 | 3 | 41 | 342.1 | 395.8 | 3.2 |
| | Grano | 23 | 5 | 11 | 4 | 5 | 52 | 295.6 | 361.0 | 3.5 |
| outer | Sturon | 34 | 2 | 22 | 3 | 7 | 31 | 117.8 | 124.2 | 1.3 |
| | Hysam | 35 | 2 | 12 | 1 | 4 | 46 | 182.5 | 190.7 | 3.5 |
| | Grano | 26 | 1 | 11 | 2 | 5 | 55 | 237.5 | 252.5 | 4.4 |
| inner | Sturon | 34 | 2 | 25 | 2 | 5 | 31 | 93.6 | 101.8 | 1.1 |
| | Hysam | 28 | 2 | 24 | 2 | 12 | 33 | 103.2 | 109.6 | 1.3 |
| | Grano | 37 | 2 | 23 | 1 | 7 | 30 | 104.0 | 112.6 | 1.2 |
| whole | Sturon | 29 | 2 | 20 | 2 | 12 | 35 | 112.4 | 124.4 | 1.6 |
| | Hysam | 40 | 2 | 12 | 1 | 4 | 41 | 194.6 | 202.8 | 3.1 |
| | Grano | 41 | 2 | 11 | 1 | 3 | 42 | 214.3 | 227.4 | 3.5 |

^a Data expressed as percentaged of total sugars.

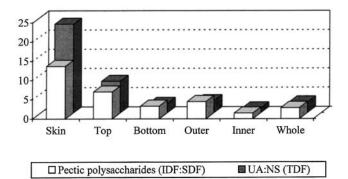


Figure 1. Distribution of pectic polysaccharides related to the UA:NS ratio.

Moreover, it was observed that the soluble fraction showed higher amounts of branched pectic polysaccharides than the insoluble fraction in all tissues, because of the minor UA:NS ratios of soluble fraction. This fact suggests that galactan chains bring about the solubilization of pectic polysaccharides. In this sense, as pectic polysaccharide branches increased in TDF of onion tissues, higher percentages of them were found in the SDF fraction (Figure 1). These results confirm the solubilization role attributed to galactan chains.

This study found important differences in DF content between onion tissues. An increasing trend in DF level from inner to outer tissues was shown, opposite the behavior of the SDF: IDF ratio. According to this, two outer leaves and brown skin submitted to technological processes could be used as good sources of dietary fiber. Hence, important differences in physiological and specific nutritional effects of fiber obtained from onion tissues should be explored. Moreover, some differences between DF components of onion tissues were noted; fleshy tissues showed highly branched soluble pectic polysaccharides, whereas brown skin was mainly constituted by homogalacturonans, decreasing the water solubilization of DF from inner to outer tissues.

ABBREVIATIONS USED

DM, dry matter; IDF, insoluble dietary fiber; SDF, soluble dietary fiber; TDF, total dietary fiber; UA:NS, ratio of uronic acids to neutral sugars.

LITERATURE CITED

- Hanelt, P. Taxonomy, evolution and history. In *Onions and Allied Crops*; Brewster, J. L., Rabinowitch, H. D., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. I, pp 1–26.
- (2) Ernst, M. K.; Chatterton, J.; Harrison, P. A.; Matitschka, G. Characterization of fructan oligomers from species of the genus *Allium L. J. Plant Physiol.* **1998**, *153*, 53–60.
- (3) Augusti, K. T. Therapeutic and Medicinal Values of Onion and Garlic. In *Onions and Allied Crops*; Brewster, J. L., Rabinowitch, H. D., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. III, pp 93–108.
- (4) Ng, A.; Smith, A. C.; Waldron K. W. Effect of tissue type and variety on cell wall chemistry of onion (*Allium cepa L.*). *Food Chem.* **1998**, *63* (1), 17–24.
- (5) Prince, C. L.; Shuler, M. L. Altering flavor profiles in onion (*Allium cepa* L.) root cultures through directed biosynthesis. *Biotechnol. Prog.* 1997, 13, 506–510.
- (6) Kubec, R.; Drhová, V.; Velíšek, J. Volatile compounds thermally generated from S-propylcysteube and S-propylcysteine sulfoxidearoma precursors of Allium vegetables. J. Agric. Food Chem. 1999, 47, 1132–1138.

- (7) Price, K. R.; Bacon, J. R.; Rhodes, M. J. C. Effect of storage and domestic processing on the content and composition of flavonol glucosides in onion (*Allium cepa*). J. Agric. Food Chem. **1997**, 45, 938–942.
- (8) Hirota, S.; Shimoda, T.; Takahama, U. Tissue and spatial distribution of flavonol and peroxidase in onion bulbs and stability of flavonol glucosides during boiling of the scales. J. Agric. Food Chem. 1998, 46, 3497–3502.
- (9) Redgwell, R. J.; Selvendran, R. R. Structural features of cell wall polysaccharides of onion. *Carbohydr. Res.* **1986**, *157*, 183– 199.
- (10) Patil, B. S.; Pike, L. M. Distribution of quercetin in different rings of various coloured onions (*Allium cepa L.*) cultivars. J. *Hortic. Sci.* **1995**, 70, 643–650.
- (11) Lintas, C.; Cappelloni, M. Content and composition on dietary fiber in raw and cooked vegetables. *Food Sci. Nutr.* **1988**, *42*, 117–124.
- (12) Fenwick, G. R.; Hanley, A. B. Chemical composition. In *Onions and Allied Crops, Vol. III, Biochemistry Food Science and Minor Crops*; Brewster, J. L., Rabinowitch, H. D., Eds.; CRC Press: Boca Raton, FL, 1990; pp 17–32.
- (13) Kontraszki, M.; Hudson, G. J.; Englyst, H. N. Dietary fiber in Hungarian foods measured by the Englyst NSP procedure and the AOAC Prosky procedure: a comparison study. *Food Chem.* **1999**, *64*, 445–450.
- (14) Ishii, S. Enzymic extraction and linkage analysis of pectic polysaccharides from onion. *Phytochemistry* **1981**, *21*, 778–780.
- (15) Ryden, P.; Colquhoun, I. J.; Selvendran, R. R. Investigations of structural features of the pectic polysaccharides of onion by ¹³C N.M.R. spectroscopy. *Carbohydr. Res.* **1989**, *185*, 233–237.
- (16) Ha, M. A.; Apperley D. C.; Jarvis, M. C. Molecular rigidity in dry and hydrates onion cell walls. *Plant Physiol.* **1997**, *115*, 593– 598.
- (17) Maw, B. W.; Hung, Y. C.; Tollner, E. W.; Smittle, D. A.; Mullinix, B. G. Physical and mechanical properties of fresh and stored sweet onions. *Trans. ASAE* **1996**, *39* (2), 633–637.
- (18) Sinclair, P. J.; Blakeney, A. B.; Barlow, E. W. R. Relationships between bulb dry matter content, soluble solids concentration and non-structural carbohydrate composition in the onion (*Allium cepa*). J. Sci. Food Agric. **1995**, 69, 203–209.
- (19) Jaime, L.; Martín-Cabrejas, M. A.; Mollá, E.; López-Andréu, F. J.; Esteban, R. M. Effect of storage on fructan and fructooligosaccharide of onion (*Allium cepa L.*). J. Agric. Food Chem. 2001, 49, 982–988.
- (20) AOAC. *Official Methods of Analysis*, 16th ed.; Association of Official Analytical Chemists: Washington, DC, 1995.
- (21) Martín-Cabrejas, M. A.; Jaime, L.; Karanja, C.; Downie, A. J.; Parker, M. L.; López-Andréu, F. J.; Maina, G.; Esteban, R. M.; Smith, A. C.; Waldron, K. W. Modifications to physicochemical and nutritional properties of hard-to-cook beans (*Phaseolus vulgaris* L.) by extrusion cooking. *J. Agric. Food Chem.* **1999**, 47, 1174–1182.
- (22) Jaime, L. Análisis de carbohidratos en bulbos de cebolla (Allium cepa L.). Aprovechamiento Como Fuente de Fibra Alimentaria; Universidad Autónoma de Madrid: Madrid, Spain, 2000; pp 228–242.
- (23) Blumenkrantz, N.; Asboe-Hensen, G. New method for quantitative determination of uronic acids. *Anal. Biochem.* 1973, 54, 484–489.
- (24) Bender, F. E.; Douglass, L. W.; Kramer, A. Statistical Methods for Food and Agriculture; Bender, F. E., Douglass, L. W., Kramer, A., Eds.; Food Products Press: New York, 1989.
- (25) Luh, B. S.; Somogyi, L. P.; Meehan, J. J. Vegetable dehydration. In *Commercial Vegetable Processing*; Luh, B. S., Woodroof, J. P., Eds.; AVI Publishing: Westport, CT, 1975; pp 361–415.
- (26) Lancaster, J. E.; Reay, P. F.; Mann, J. D.; Bennett, W. D.; Sedcole, R. Quality in New Zealand-grown onion bulbs—survey of chemical and physical characteristics. *N. Z. J. Exp. Agric.* **1988**, *16*, 279–285.

- (27) Rutherford, P. P.; Whittle, R. The carbohydrate composition of onions during long-term cold storage. J. Hortic. Sci. 1982, 57 (3), 349–356.
- (28) Nieuwhof, M.; Bruyn, J. W.; Garretsen, F. Methods to determine solidity DM content of onions (*Allium cepa* L.). *Euphytica* 1973, 22, 39–47.
- (29) Nilsson, T. The influence of the time of harvest on the chemical composition of onions. Swed. J. Agric. Res. 1980, 10, 77–88.
- (30) Olson, A.; Gray, G. M.; Chiu, M.-C. Chemistry and analysis of soluble dietary fiber. *Food Technol.* **1987**, Feb, 71–80.
- (31) Jaime, L.; Martínez, F.; Martín-Cabrejas, M. A.; Mollá, E.; López-Andréu, F. J.; Waldron, K. W.; Esteban, R. M. Total fructan and fructooligosaccharide content in different onion tissues. J. Food Sci. Agric. 2001, 81, 177–182.
- (32) Christensen, E. H. Characteristics of sugarbeet fiber allow many food uses. *Cereal Foods World*. **1989**, *34* (7), 541–544.
- (33) Anderson, J. W.; Bridges, S. R. Dietary fibre content of select foods. Am. J. Clin. Nutr. 1988, 47, 440–447.

- (34) Esteban, R. M.; Mollá, E.; Valiente, C.; Jaime, L.; López-Andréu, F. J.; Martín-Cabrejas, M. A. Dietary fibre: Chemical and physiological aspects. *Recent Res. Dev. Agric. Food Chem.* **1998**, 2, 293–308.
- (35) Martín-Cabrejas, M. A.; Waldron, K.; Selvendran, R. R.; Parker, M. L.; Moates, G. K. Ripening-related changes in the cell walls of Spanish pear. *Physiol. Planta.* **1994**, *91*, 671–676.
- (36) Guijarro, A. Estudio analítico de la fibra alimentaria en cebolla (*Allium cepa* L.). M.Sc. Universidad Autónoma de Madrid, Spain, 1999; p 155.

Received for review June 25, 2001. Revised manuscript received October 9, 2001. Accepted October 9, 2001. This work has been carried out with financial support from the European Union (FAIR-CT96-1184).

JF010797T