

Binding Capacity of 18 Fiber Sources for Calcium

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Eighteen fiber sources were analyzed for protein, phytic acid (PA), soluble (SF) and insoluble (IF) fiber, total dietary fiber, water-holding capacity (WHC), and endogenous calcium concentration. Calcium-binding capacity (CaBC) was determined in acid-washed fiber sources. Protein content varied from 0.0% in cane fiber and cellulose to 22.2% in tomato fiber. Acid-wash treatment significantly ($P < 0.05$) reduced the protein content. PA in acid-washed samples ranged from 0 $\mu\text{g/g}$ of sample in cane fiber, cellulose, corn bran, and orange fiber to 15 312 $\mu\text{g/g}$ of sample in rice bran. SF ranged from 1.9% in corn bran to 28.3% in orange fiber. IF varied from 34.9% in orange fiber to 87.0% in cellulose. WHC ranged from 2.36% in oat fiber to 10.85% in sugar beet fiber. Endogenous calcium varied from 304 $\mu\text{g/g}$ of sample in cane fiber to 12 432 $\mu\text{g/g}$ of sample in orange fiber. CaBC ranged from a low of 480 $\mu\text{g/g}$ of sample for cellulose to a high of 20 137 $\mu\text{g/g}$ of sample for orange fiber. No relationship was found between protein, PA, SF, IF, WHC, and CaBC.

INTRODUCTION

The data for human consumption of fiber and its effect on calcium bioavailability are of mixed results. An early study demonstrated that the feeding of whole wheat flour caused a negative calcium balance (McCance and Widdowson, 1942). A later study found that increasing wheat fiber from 22 to 53 g/day resulted in a negative calcium balance (Cummings et al., 1979b). Studies conducted in the Middle East found that when bread was consumed with or without phytate present, only the fiber and not the phytate had an effect on calcium balance (Reinhold et al., 1973). Kelsay et al. (1979) found that the addition of fruits and vegetables to a normal diet caused a negative balance to occur. Dintzis et al. (1985) found that humans consuming 26 g/day of corn bran, wheat bran, and soybean hulls had increased fecal calcium excretion. There are other studies which demonstrate that dietary fiber has no or a very limited effect upon calcium balance in humans. Cummings et al. (1979b) reported that addition of 36 g of pectin/day in the diet of five healthy students for 9 weeks had no overall effect on calcium balance. Similarly, Behall et al. (1987) showed that consumption of 7.5 g of cellulose, locust bean, or karaya gum per 1000 calories for 4 weeks had no significant effect on the mineral balance of calcium.

Many problems arise when trying to compare the results from different human studies because of the variation of fiber type and amount fed, the length of study, and the presence of other dietary components capable of binding minerals. Fibers need to be investigated by an *in vitro* method to determine their cation-exchange capacity.

Dietary fibers have a cation-exchange capacity and, therefore, the potential of reducing the bioavailability of dietary minerals. The fiber can bind the minerals in the small and/or large intestinal tract leading to increased fecal excretion of minerals and electrolytes (Reinhold et al., 1975; Sandstead et al., 1979; Kelsay, 1979; Rendleman, 1982; Clydesdale, 1983). The functional capacity of certain dietary fibers to behave as a cation exchanger has been established by Kay (1982), Thompson and Weber (1979, 1981), and Platt and Clydesdale (1987). *In vitro* exper-

iments have found that the fiber sources varied greatly in binding capacity. The mechanism of the binding is theorized as being caused by several possible sources. Uronic acid content of the diet has been proposed as a possible binder of calcium (James et al., 1978). Phytate was proposed as the major cation-binding agent in several studies (Rendleman, 1982; Rendleman and Grobe, 1982). Various components of dietary fiber such as cellulose, hemicellulose, pectin, and lignin have been proposed as cation binders. Investigators have found that hemicellulose, α -cellulose, pH, and heat treatment did affect the binding of certain minerals (Camine and Clydesdale, 1981; Mod et al., 1983). However, Rendleman (1982) demonstrated that cellulose, starch, hemicellulose, pectin, and protein had little affinity for calcium at a neutral pH. Pectin was found to have little cation affinity for calcium at a pH of either 3.2 or 7.2 (Nikdel et al., 1991). The cation-binding capacity of fiber sources has been shown in other studies to be pH dependent.

pH has been shown by several investigators as the most important factor in the binding of minerals. Thompson and Weber (1979, 1981) determined by an *in vitro* method that at a low pH (1.0-2.0), little endogenous mineral remained or could be bound by fiber sources, while at pH 6.8, most minerals were either bound or were somehow complexed by several fiber sources. Camine and Clydesdale (1981) concluded that pH, as well as fiber type and treatment, determined the ability of minerals to complex with the fiber. They found that lignin would bind substantial amounts of calcium, zinc, iron, and magnesium, while cellulose bound only a very small amount of these minerals. The number and strength of binding sites of lignin, cellulose, and pectin have been studied (Platt and Clydesdale, 1987). The literature has conflicting data concerning whether fibers can bind divalent cations.

The purpose of this study is to investigate the relationship between protein content, phytic acid level, soluble and insoluble fiber, total dietary fiber, water-holding capacity, and calcium-mineral-binding capacity for 18 fiber sources. The total calcium-binding capacity of the 18 fiber sources was determined at pH 7.0.

MATERIALS AND METHODS

Materials. Eighteen fibers from fruit, vegetable, and cereal sources were evaluated as follows: (1) apple fiber (Canadian

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Table I. Protein and Ash Values of the 18 Fiber Sources after Being either Defatted (DF) or Defatted and Acid Washed (DAWF)^a

| fiber source | protein, ^b g/100 g | | ash, g/100 g | |
|---------------------------------|-------------------------------|---------------------------|---------------------------|---------------------------|
| | DF | DAWF | DF | DAWF |
| apple fiber | 4.65 ± 0.24 ^A | 3.97 ± 0.04 ^A | 11.11 ± 0.06 ^A | 10.93 ± 0.07 ^A |
| barley fiber | 11.80 ± 0.19 ^A | 8.54 ± 0.12 ^B | 6.97 ± 0.14 ^A | 4.84 ± 0.05 ^B |
| cane fiber | 0.00 ± 0.00 ^A | 0.00 ± 0.00 ^A | 0.83 ± 0.08 ^A | 0.43 ± 0.36 ^A |
| cellulose | 0.00 ± 0.00 ^A | 0.00 ± 0.00 ^A | 0.42 ± 0.10 ^A | 0.00 ± 0.00 ^B |
| corn bran | 3.64 ± 0.14 ^A | 3.45 ± 0.04 ^B | 1.27 ± 0.01 ^A | 0.11 ± 0.03 ^B |
| oat hulls | 3.51 ± 0.03 ^A | 2.14 ± 0.06 ^B | 6.07 ± 0.01 ^A | 5.06 ± 0.04 ^B |
| oat fiber | 0.00 ± 0.00 ^A | 0.00 ± 0.00 ^A | 2.45 ± 0.07 ^A | 1.33 ± 0.04 ^B |
| oat fiber, bleached | 0.00 ± 0.00 ^A | 0.00 ± 0.00 ^A | 2.07 ± 0.20 ^A | 1.57 ± 0.28 ^A |
| orange fiber | 5.29 ± 0.01 ^A | 5.41 ± 0.04 ^A | 3.72 ± 0.15 ^A | 2.01 ± 0.02 ^B |
| pea fiber (Centara) | 4.80 ± 0.24 ^A | 3.38 ± 0.02 ^B | 1.97 ± 0.16 ^A | 0.09 ± 0.12 ^B |
| pea fiber (Dupro) | 3.52 ± 0.06 ^A | 2.21 ± 0.15 ^B | 4.03 ± 0.06 ^A | 0.05 ± 0.01 ^B |
| peanut fiber | 15.90 ± 0.03 ^B | 16.63 ± 0.10 ^A | 2.72 ± 0.07 ^A | 0.42 ± 0.06 ^B |
| rice bran | 19.74 ± 0.18 ^B | 24.06 ± 0.09 ^A | 12.32 ± 0.16 ^A | 1.38 ± 0.10 ^B |
| soy bran (Nutrisoy) | 8.58 ± 0.02 ^A | 7.58 ± 0.36 ^A | 4.32 ± 0.13 ^A | 0.42 ± 0.05 ^B |
| soybean fiber | 9.09 ± 0.47 ^A | 5.91 ± 0.42 ^B | 4.33 ± 0.04 ^A | 0.36 ± 0.07 ^B |
| sugar beet fiber | 8.60 ± 0.08 ^A | 8.07 ± 0.03 ^B | 4.66 ± 0.04 ^A | 0.86 ± 0.06 ^B |
| tomato fiber | 22.22 ± 0.42 ^A | 20.82 ± 0.45 ^B | 4.93 ± 0.08 ^A | 1.51 ± 0.00 ^B |
| wheat bran, AACC hard red wheat | 16.88 ± 0.93 ^A | 17.44 ± 0.13 ^A | 6.80 ± 0.02 ^A | 0.35 ± 0.03 ^B |

^a Determined on duplicate fat-free dry samples (means ± SD). ^b Expressed as N × 6.25. Mean values having the same superscript within rows are not significantly different ($P < 0.05$).

Harvest, Ontario, Canada), (2) barley fiber (Canadian Harvest, Ontario, Canada), (3) cane fiber (Canadian Fibre Foods, Inc., British Columbia, Canada), (4) cellulose (ICN Pharmaceuticals, Inc., Staten Island, NY), (5) corn bran (Canadian Harvest, Ontario, Canada), (6) oat hulls (National Oat Co., Cedar Rapids, IA), (7) oat fiber (Canadian Harvest, Ontario, Canada), (8) oat fiber, bleached (Canadian Harvest, Ontario, Canada), (9) orange fiber (D. D. Williamson & Co., Modesto, CA), (10) pea fiber "Centara" (Mid America Food Sales LTD, Northbrook, IL), (11) pea fiber "Dupro" (Dupro Division, Golden Valley, MN), (12) peanut fiber (Canadian Harvest, Ontario, Canada), (13) rice bran fiber (California Natural Products, Lathrop, CA), (14) soybean bran "Nutrisoy" (Archer Daniels Midland Co., Decatur, IL), (15) soybean fiber (Archer Daniels Midland Co., Decatur, IL), (16) sugar beet fiber (Amalgamated Sugar Co., Twin Falls, ID), (17) tomato fiber (Canadian Harvest, Ontario, Canada), and (18) certified hard red wheat bran (AACC, St. Paul, MN).

Sample Preparation. Twenty grams of various fiber samples were first defatted by Soxhlet using hexane as a solvent, freeze-dried, and then ground in a hammer mill until all samples passed through U.S. standard screen number 20 (0.0331 in.). A 0.5-g sample was taken for analysis of endogenous calcium concentration. The endogenous minerals were removed by shaking a 1% HCl/fiber mixture (1:20 ratio of fiber to 1% HCl solution, w/v, pH < 2) for a period of 3 h. The samples were filtered through coarse fritted glass funnels and then repeatedly washed using distilled deionized water until a pH of 7 was achieved. The covered washed fiber material was dried by air current on a laboratory bench top until dry. A 0.5-g sample of the acid-washed material was taken for calcium analysis. The total binding capacity of a material was determined by weighing a 10-g sample of acid-washed fiber mixed with a 1 M calcium chloride solution in a ratio of 1:100 w/v. The slurry was mixed on a shaker overnight in acid-washed bottles (Rockway et al., 1987). The slurry was filtered and repeatedly washed with distilled deionized water (pH = 7) and then freeze-dried. A 0.5-g sample was taken for calcium analysis. The remaining portion of the sample was acid washed, distilled deionized water washed, and dried. A 0.5-g sample was taken for calcium analysis.

Protein and Ash Determination. Duplicate fat-free and acid-washed samples of the 18 fiber samples were analyzed for protein and ash using AOAC (1990) 984.13 and 923.03 methods, respectively.

Phytic Acid Analysis. Samples from the 18 fiber sources were analyzed for phytic acid (PA) using the AOAC (1990) 986.11 method. PA concentration calculated as milligrams per gram of sample was determined colorimetrically at 640 nm using a Sequoia-Turner spectrophotometer.

Dietary Fiber Determination. The soluble and insoluble fibers were determined in duplicate fat-free dry samples using

the method of Prosky et al. (1988). After completion of the incubation steps using enzymes, we filtered the insoluble fiber and dried it in an oven. This step separated the insoluble fiber residue from the solvent containing the soluble fiber. The soluble fiber was precipitated by the addition of 95% alcohol (1:4 ratio of fiber to alcohol) overnight. The soluble fiber was separated by filtration and then dried in an oven. Samples of insoluble and soluble fibers were analyzed for protein and ash and these results subtracted from the total fiber residues (Prosky et al., 1988). Total dietary fiber (TDF) was calculated by the addition from the data of soluble and insoluble fiber.

Water-Holding Capacity. Duplicate fat-free dry samples from the 18 fiber sources were evaluated for water-holding capacity by the centrifugation method (AACC 88-04, 1983). Into centrifuge tubes was placed a quantity of weighed material (1 g), and a volume of distilled deionized water was added (30 mL). The contents were mixed and centrifuged (2000 g for 10 min), the supernatant was decanted, and then the amounts of water held per gram of fiber material was calculated.

Calcium Analysis. Various acid-washed fiber samples were taken for calcium analysis from ground defatted, acid-washed, Ca-bound, and re-acid-washed material. Duplicate fat-free dry samples were weighed in 0.5-g lots and wet ashed using the AOAC (1990) 968.08 method. Acid-digested samples were quantitatively transferred and made up to a given volume for calcium determinations by flame atomic absorption spectrophotometry (Hitachi 180-70). The standard solutions were prepared daily from a certified atomic absorption standard (Fisher Scientific, NJ). Standard and sample solutions contained lanthanum at a 1% concentration to mask interference by phosphorus. Standard curves were determined after every 10 samples with average correlation coefficients of 0.99995. Precision was determined within runs (<5%) and between runs (<10%). All glassware was acid washed in 50% HNO₃ and rinsed three times in distilled deionized water.

Statistical Analysis. Data, determined in duplicate fat-free dry samples, were statistically analyzed using the one-way analysis of variance with means separated and least-significance difference at $P < 0.05$ for the fiber samples (Steel and Torrie, 1960).

RESULTS AND DISCUSSION

Protein and Ash Contents. Protein and ash contents of the 18 fiber sources are presented in Table I. Tomato fiber, rice bran, wheat bran, and peanut fiber showed higher protein content than the remaining fiber sources. Similar values were reported for AACC certified wheat bran, rice bran, soy bran (Nutrisoy), and oat and barley hulls (Parrot and Thrall, 1978). Acid-wash treatment significantly

Table II. Phytic Acid Content of the 18 Acid-Washed Fiber Sources^a

| fiber source | phytic acid, $\mu\text{g/g}$ |
|---------------------------------|--------------------------------|
| apple fiber | 1354 \pm 116 ^{CD} |
| barley fiber | 4529 \pm 857 ^C |
| cane fiber | 0 \pm 0 ^D |
| cellulose | 0 \pm 0 ^D |
| corn bran | 0 \pm 0 ^D |
| oat hulls | 366 \pm 81 ^D |
| oat fiber | 0 \pm 0 ^D |
| oat fiber, bleached | 272 \pm 77 ^D |
| orange fiber | 0 \pm 0 ^D |
| pea fiber (Centara) | 487 \pm 64 ^D |
| pea fiber (Dupro) | 780 \pm 192 ^{CD} |
| peanut fiber | 1670 \pm 217 ^{CD} |
| rice bran | 15312 \pm 6594 ^A |
| soy bran (Nutrisoy) | 1042 \pm 168 ^{CD} |
| soybean fiber | 665 \pm 14 ^{CD} |
| sugar beet fiber | 203 \pm 68 ^D |
| tomato fiber | 8535 \pm 4097 ^B |
| wheat bran, AACC hard red wheat | 12174 \pm 2032 ^{AB} |

^a Determined in duplicate fat-free acid-washed dry samples. Mean values with the same superscript within the column are not significantly different ($P < 0.05$).

Table III. Soluble, Insoluble, and Total Dietary Fiber Values for the 18 Fiber Samples^a

| fiber source | soluble fiber, g/100 g | insoluble fiber, g/100 g | total dietary fiber, g/100 g |
|---------------------------------|------------------------|--------------------------|------------------------------|
| apple fiber | 12.0 | 49.6 | 61.6 |
| barley fiber | 3.5 | 57.1 | 60.6 |
| cane fiber | 4.2 | 58.0 | 62.2 |
| cellulose | 4.4 | 87.0 | 91.4 |
| corn bran | 1.9 | 79.1 | 81.0 |
| oat hulls | 5.0 | 69.6 | 74.6 |
| oat fiber | 3.2 | 70.9 | 74.1 |
| oat fiber, bleached | 1.2 | 89.0 | 90.2 |
| orange fiber | 28.3 | 34.9 | 63.3 |
| pea fiber (Centara) | 9.8 | 78.8 | 88.4 |
| pea fiber (Dupro) | 10.8 | 77.4 | 88.2 |
| peanut fiber | 4.5 | 59.9 | 64.4 |
| rice bran | 4.5 | 29.5 | 34.0 |
| soy bran (Nutrisoy) | 10.5 | 61.4 | 71.8 |
| soybean fiber | 8.6 | 69.5 | 78.1 |
| sugar beet fiber | 14.8 | 62.7 | 77.5 |
| tomato fiber | 6.7 | 60.2 | 66.9 |
| wheat bran, AACC hard red wheat | 6.4 | 47.2 | 53.6 |

^a Determined in duplicate fat-free dry samples.

decreased protein content in most fiber sources. In rice bran and peanut fiber, protein content increased probably because of the loss of soluble carbohydrates (soluble fibers). Ash content decreased significantly in all acid-washed fiber sources (Table I). Acid-wash treatment appeared more efficient in reducing ash content than protein content.

Phytic Acid. Cane fiber, cellulose, corn bran, oat fiber, and orange fiber showed no phytic acid (PA) after acid-wash treatment (Table II). Rice and wheat bran had, however, significantly higher amounts of PA when compared to the other fiber sources. PA concentration varied widely in the remaining fiber sources.

Soluble and Insoluble Fiber. Table III lists the data for soluble (SF), insoluble (IF), and total dietary fiber (TDF). The SF values ranged from a low of 1.2% for bleached oat fiber to a high of 28.3% for orange fiber. The IF ranged from a low of 29.5% for rice bran to a high of 87.0% for cellulose. The TDF values ranged from a low of 34.0% for rice bran to a high of 91.4% for cellulose. These TDF values agreed with published data for various fiber sources, either raw or treated including barley, corn, peanut, sugar beet, and wheat (Dreher, 1987).

Water-Holding Capacity. The fiber samples varied for water-holding capacity (WHC) from 2.08 g/g for peanut

Table IV. Water-Holding Capacity (WHC) Values for the 18 Fiber Samples Compared with Values from the Literature^a

| fiber source | WHC, g/g | WHC, ^b g/g |
|----------------------------|----------|-------------------------------------|
| apple fiber | 5.38 | 2.3 ^f -3.4 ^e |
| barley fiber | 3.37 | 3.3 ^e |
| cane fiber | 7.42 | |
| cellulose | 3.56 | 3.4 ^d |
| corn bran | 3.34 | 2.5 ^f -5.0 ^d |
| oat hulls | 4.34 | 3.8 ^e |
| oat fiber | 2.36 | 1.4 ^f |
| oat fiber, bleached | 3.28 | |
| orange fiber | 7.67 | 5.7 ^f -28.2 ^d |
| pea fiber (Centara) | 3.13 | 4.6 ^f |
| pea fiber (Dupro) | 2.55 | 8.0 ^d |
| peanut fiber | 2.08 | 2.4-4.1 ^f |
| rice bran | 3.00 | 1.0 ^e -9.7 ^d |
| soy bran (Nutrisoy) | 4.23 | 12.0 ^f |
| soybean fiber | 5.67 | 2.4 ^f |
| sugar beet fiber | 10.85 | 28.7 ^f |
| tomato fiber | 3.07 | 10.7 ^f |
| wheat bran, AACC red wheat | 5.04 | 2.6 ^f -8.5 ^d |

^a Determined in duplicate fat-free dry samples. ^b Data from literature. ^c Parrot and Thrall (1978). ^d Schaller (1978). ^e Schimberni et al. (1982). ^f Dreher (1987).

fiber to 10.85 g/g for sugar beet fiber (Table IV). Three fibers, cane, orange, and sugar beet fiber, exceeded a WHC of 7 g/g. The other 15 fiber samples were 5 g/g or less in WHC. Depending on the method used, different WHC values have been reported in literature. Our results generally agree with data cited in literature particularly when similar methods were used (Table IV). The chemical composition of fiber plays a role in its ability to hold water. Cellulose and lignin tend to have low WHC values, while hemicellulose and pectin have high WHC values (Rasper, 1979). The high WHC values for sugar beet fiber (14.8 g/g SF) and orange fiber (28.3 g/g SF) appear to be related to their high concentration of soluble fiber, while apple fiber (12.0 g/g SF) and soybean bran (10.5 g/g SF), which have high soluble fiber values, had moderate WHC values.

Total Calcium-Binding Capacity. The 18 fiber sources varied greatly in their endogenous calcium concentrations ranging from a low of 85 $\mu\text{g/g}$ for corn bran to a high of 12 432 $\mu\text{g/g}$ for orange fiber (Table V). The material analyzed after being acid washed showed an excellent removal of calcium ions with the exception of the orange fiber. The fibers ranged from 3 to 278 $\mu\text{g/g}$ with the exclusion of the orange fiber which bound 10 110 $\mu\text{g/g}$. The orange fiber tightly bound calcium ions and lost only 2288 $\mu\text{g/g}$ while retaining more than 10 135 $\mu\text{g/g}$. This would indicate that a different type of binding was involved to retain tightly the 10 000+ $\mu\text{g/g}$ of calcium ions. James et al. (1978) have shown that *in vitro* calcium binding in fiber was not only related to fiber source but also directly proportional to the amount of uronic acid present in the sample. This may explain the high amount of calcium bound in our orange fiber. The other fibers readily released their calcium ions at a pH less than 1. This confirms the prior data of Thompson and Weber (1979 and 1981) who found that a low pH of 1 would remove divalent ions from various fiber sources. The total calcium ions bound was found to range from a low of 480 $\mu\text{g/g}$ for cellulose to a high of 20 137 $\mu\text{g/g}$ for the orange fiber (Table V). Five of the fiber sources had a high binding capacity with values which were greater than 9000 $\mu\text{g/g}$ with the exclusion of the orange fiber. These were tomato fiber, both soybean fiber and bran, sugar beet fiber, and peanut fiber. There appeared to be no logical explanation for which types of fibers bound high concentrations of calcium. For example, neither the vegetables or the fruits were consistent in either

Table V. Total Calcium-Binding Capacity by the 18 Fiber Sources^a

| source | calcium concn, $\mu\text{g/g}$ | | | |
|--------------------------------|--------------------------------|------------------------------|------------------------------|----------------|
| | endogenous | acid-washed | total bound | re-acid-washed |
| apple fiber | 1253 \pm 85 ^{JK} | 73 \pm 3 ^{CD} | 3896 \pm 81 ^H | 73 \pm 3 |
| barley fiber | 1164 \pm 207 ^K | 22 \pm 2 ^D | 5393 \pm 435 ^F | 49 \pm 5 |
| cane fiber | 304 \pm 1 ^M | 11 \pm 4 ^D | 880 \pm 111 ^K | 13 \pm 2 |
| cellulose | 427 \pm 4 ^M | 10 \pm 1 ^D | 480 \pm 50 ^K | 45 \pm 2 |
| corn bran | 85 \pm 1 ^N | 3 \pm 1 ^D | 4697 \pm 103 ^G | 65 \pm 2 |
| oat hulls | 1665 \pm 40 ^I | 5 \pm 1 ^D | 2159 \pm 18 ^J | 21 \pm 1 |
| oat fiber | 2159 \pm 21 ^H | 15 \pm 1 ^D | 2060 \pm 0 ^J | |
| oat fiber, bleached | 1564 \pm 35 ^I | 18 \pm 2 ^D | 2740 \pm 543 ^I | 6 \pm 1 |
| orange fiber | 12432 \pm 83 ^A | 10110 \pm 329 ^A | 20137 \pm 221 ^A | 2467 \pm 71 |
| pea fiber (Centara) | 4731 \pm 21 ^C | 190 \pm 9 ^{BC} | 7121 \pm 167 ^E | 138 \pm 0 |
| pea fiber (Dupro) | 4862 \pm 40 ^C | 161 \pm 1 ^{BCD} | 5669 \pm 18 ^F | 45 \pm 1 |
| peanut fiber | 3293 \pm 0 ^F | 23 \pm 1 ^D | 15000 \pm 117 ^B | 63 \pm 1 |
| rice bran | 755 \pm 22 ^L | 22 \pm 1 ^D | 747 \pm 6 ^K | 115 \pm 13 |
| soy bran (Nutrisoy) | 4409 \pm 37 ^D | 75 \pm 10 ^{CD} | 10884 \pm 62 ^C | 97 \pm 7 |
| soybean fiber | 5449 \pm 1 ^B | 117 \pm 7 ^{BCD} | 10798 \pm 280 ^C | 120 \pm 4 |
| sugar beet fiber | 4252 \pm 0 ^E | 278 \pm 3 ^B | 9393 \pm 20 ^D | 39 \pm 1 |
| tomato fiber | 2964 \pm 16 ^G | 124 \pm 49 ^{BCD} | 9240 \pm 139 ^D | 124 \pm 49 |
| wheat bran, AAC hard red wheat | 1332 \pm 40 ^J | 100 \pm 21 ^{CD} | 7308 \pm 10 ^E | 100 \pm 21 |

^a Determined on duplicate fat-free dry samples (means \pm SD). Mean values having the same superscript within columns are not significantly different ($P < 0.05$).

binding or not binding calcium ions. It has been proposed the hemicellulose and lignin are the most chemically active components of the cell wall and therefore responsible for decreasing bioavailability of nutrients (Sosulski and Cadden, 1982).

The re-acid-washing of the fiber samples after being bound with calcium exhibited ranges of residual calcium from 6 $\mu\text{g/g}$ for oat fiber to 138 $\mu\text{g/g}$ for pea fiber (Dupro) (Table V). An exception, orange fiber, had a residual calcium concentration of 2467 $\mu\text{g/g}$ of sample. The fiber samples demonstrated their ability to again release bound calcium ions when exposed to an acid pH. This reaffirms the weak bond that the fiber samples had for the calcium ion and its removal of calcium from the fiber samples by a low pH. Fiber has the ability to bind divalent ions but is very pH dependent (Thompson and Weber, 1981; Camine and Clydesdale, 1981).

The cation-exchange capacity (CEC) method used in the current study was similar to the method of Van Soest et al. (1965) but was not similar to the one used by Ebihara and Takeuchi (1991). This is the major problem in trying to compare data from different laboratories using different methodologies in determining CECs.

Correlation Coefficients between the Variables Studied. Coefficient correlations (r) between the different variables studied are indicated in Table VI. Neither protein nor phytic acid were correlated to total calcium bound (Table VI). There appears to be also no clear relationship between SF concentration and WHC with a correlation coefficient of 0.642. Correlation coefficients between TDF and WHC (-0.145) and IF and WHC (-0.404) were not significant (Table VI). Using hemicellulose values cited in literature (Schaller, 1978; Dreher, 1989; Tjebbes, 1989) we calculated a correlation coefficient between WHC and hemicellulose. No relationship between the two variables was found ($r = 0.054$). Fibers with a high concentration of hemicellulose did not necessarily have high WHC. There must be a more complex mechanism in fibers that determines its WHC than just their hemicellulose and pectin concentrations. Investigating further

Table VI. Correlation Coefficients of Protein, Phytic Acid, Water-Holding Capacity (WHC), Dietary Fiber, and Calcium Total Binding Capacity (CaTBC)

| dependent variable | independent variable | regression | r^2 |
|--------------------|----------------------------|-----------------------|--------|
| protein | total calcium bound | $y = 200.5x + 5104$ | 0.201 |
| phytic acid | total calcium bound | $y = -0.101x + 6944$ | -0.117 |
| WHC | total dietary fiber | $y = -0.685x + 74.56$ | -0.145 |
| WHC | soluble fiber | $y = -1870x + -1252$ | 0.642 |
| WHC | insoluble fiber | $y = -2491x + 75.64$ | -0.404 |
| WHC | hemicellulose ^b | $y = -0.008x + 4.96$ | -0.054 |
| CaTBC | WHC | $y = 555.2x + 4103$ | 0.231 |
| CaTBC | total dietary fiber | $y = -130.3x + 16061$ | -0.253 |
| CaTBC | insoluble fiber | $y = 207.6x + 19987$ | -0.531 |
| CaTBC | hemicellulose ^b | $y = -71.9x + 8189$ | -0.194 |

^a r = correlation coefficient between two variables. ^b Literature hemicellulose values used (Schaller, 1978; Breher, 1989; Tjebbes, 1989).

relationships, there appeared to be no clear relationship between protein, PA, WHC, soluble and insoluble fibers, and hemicellulose concentrations with calcium total binding capacity (Table VI). The correlation coefficient between calcium total binding capacity (CaTBC) and WHC was 0.231 versus -0.531 for insoluble fiber and -0.253 for TDF (Table VI). The fiber materials used for the total binding experiment were acid washed which theoretically should have removed the soluble fiber, soluble protein, and phytic acid contents. The insoluble fiber should have been the only material left to bind the calcium ions. However, there could have been some insoluble pectin not removed by the acid wash and involved in binding for an unknown effect. Determined phytic acid values for acid-washed fibers of pea, corn, peanut, soy, tomato, rice, apple, oats, and wheat ranged from 0.05% for peas to 1.53% for rice samples. These low values would have little or no effect in the binding of calcium ions as shown by the data for binding of Ca. Rice had the highest phytic acid concentration of 1.53% for the acid-washed fiber samples but a very low binding of Ca of 747 $\mu\text{g/g}$, while acid-washed tomato fiber had a phytic acid concentration of 0.85% but bound Ca at a level of 9240 $\mu\text{g/g}$.

If one relates the total calcium-binding data with published values for the hemicellulose for all 18 of the fibers which bound calcium, no relationship can be observed with a correlation coefficient of -0.194 (Table VI). Ebihara and Takeuchi (1991) found that particle size had no effect on CEC but pH did have a definite effect. The authors further theorized that the hemicellulose in refined corn hull consisted of a wide variety of branched polysaccharide polymers which contained polyhydroxyl and carboxyl groups. They suggested that the carboxyl group as well as the hydroxyl groups participated in the ion-exchange processes. Rice hemicellulose was found to bind calcium and subsequently release it by both pH and enzymatic affects (Mod et al., 1982; Norman et al., 1987). The authors speculated that calcium was chelated primarily between the sugars of the isolated hemicellulose. The release effect caused by a low pH suggests that minerals would be released as food passes through the stomach. However, reactions of dietary fiber studied under *in vitro* conditions may not always correlate with those existing *in vivo* because of the complex physiological and biochemical reactions which take place in the body.

In summary, acid-washed fibers from 18 sources were found to be able to bind calcium ions from low concentrations to high concentrations. Relationships between protein, PA, WHC, hemicellulose levels, and insoluble fiber concentrations and mineral binding were investigated. No

definitive relationships could be established between the above parameters. The fibers, with the exception of orange, bound the calcium ions with a weak bond which could be broken by an acid pH change. The "groups" which are binding the calcium ions were not identified.

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