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Retention of Minerals in Protein Isolates Prepared from Peanut Flours

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Atomic absorption spectroscopy or X-ray fluorescence was used to determine concentrations of the essential minerals Ca, Fe, Cu, Mn, Mg, Na, K, and Zn in defatted peanut flours and their retention in protein isolates. To compare the effects of variety and environmental factors on mineral content, several cultivars of peanuts grown in different areas were acetone-extracted to produce defatted flours. Portions of the flours were extracted with 10% NaCl at pH 7.0, and the extracts were dialyzed vs. water and freeze-dried to obtain the protein isolates. In general, those elements that may be associated with phytic acid in the flours are present in lower, but still significant, concentrations in the protein isolates.

Oilseeds are expected to play an important role in filling world needs for edible protein. This need is intensifying because of increasing world population and heightened awareness of nutritional deficiencies in today's diets. Previous research on oil-free meals from peanuts has emphasized protein quality and/or functional properties. Little attention has been given to mineral content, despite a 1971 USDA survey that showed the three most important areas of consumer interest were planning balanced meals, weight control, and knowledge of vitamin and mineral needs (Dwyer and Alston, 1976).

Galvao et al. (1976) determined the levels of 13 essential elements in raw peanuts and peanut butter. Derise et al. (1974) reported the levels of nine elements in raw and roasted peanuts. Conkerton and Ory (1976) reported a limited comparison of mineral contents of peanut flours prepared from Virginia and Spanish peanuts. No attempt was made to determine the effects of growing area on mineral composition of the flours or on retention of minerals in protein isolates prepared from them. This report compares eight essential mineral contents in peanut flours and protein isolates prepared from three cultivars of peanuts from four different growing areas.

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MATERIALS AND METHODS

Different peanut cultivars grown in four geographic areas were obtained. The cultivars examined and their growing locations are Florunner, Ga.; Starr, Ga.; Florigiant, Ga.; Starr, Va.; Florunner, Va.; Florigiant, Va.; Starr, Okla.; and Starr, Tex.

Peanut flours (50–60% protein content) were prepared from raw, blanched peanuts by acetone extraction. The flours represent about 50% of the seed on a weight basis and have a protein content of 50–60% (N × 5.46). Isolates (90–100% protein) were prepared from the defatted flours by 10% NaCl extraction at pH 7.0. Details of the preparation are given by Conkerton and Ory (1976) and by Conkerton et al. (1973). Minerals were determined by atomic absorption (AA) or X-ray fluorescence. The concentration of the element to be determined and sensitivity of the method for that element influenced the choice of analytical method.

The atomic absorption instrument was a Perkin-Elmer Model 306, equipped with the HGA-2000 graphite furnace, a Model 56 recorder, and a deuterium background corrector. A Cahn Model G electrobalance was used to weigh milligram amounts of the samples. The instrumental

Table I. Experimental Conditions for the Determination of Cu, Fe, Mn, and Zn Using the Graphite Furnace

	drying		charring		atomizing				
element	time, s	temp, °C	time, s	temp, °C	time, s	temp, °C	slit	wavelength, nm	senst.[a]
Cu	45	110	35	950	9	2500	4	324.7	50
Fe	45	110	45	950	9	2500	3	248.3	38
Mn	45	110	45	1000	10	2400	3	403	130
Zn[b]	35	100	90	450	8	2000	4	308	3575

[a] Sensitivity is expressed in pg/0.0044 absorbance units. [b] Zn D_2 on, purge automatically interrupted.

Table II. Mineral Element Contents of Peanut Flours and Isolates by X-Ray Fluorescence

			element, mg/100 g			
variety	location	form[a]	Ca	K	Mg	Na
Florunner	Ga.	F	170	1360	90	1.1
Florunner	Ga.	S	100	2430	50	0.3
Starr	Ga.	F	110	1470	40	0.3
Starr	Ga.	S	30	5	10	0.3
Florigiant	Ga.	F	110	1740	50	0.4
Florigiant	Ga.	S	90	2590	30	0.3
Starr	Va.	F	130	1150	10	
Starr	Va.	S		5		
Florunner	Va.	F	110	1320	60	0.7
Florunner	Va.	S	80	1890	20	0.4
Florigiant	Va.	F	140	1450	50	0.7
Florigiant	Va.	S	100	2200	30	0.5
Starr	Okla.	F	140	1250	70	0.9
Starr	Okla.	S	40	7	10	0.3
Starr	Tex.	F	130	1120	10	0.3
Starr	Tex.	S	80	1750	70	0.4
NBS orchard leaves, anal. value			2000	1430	620	8.2
NBS orchard leaves, certified value			2090 ± 30	1470 ± 30	620 ± 20	8.2 ± 0.6

[a] F, flour; S, isolate.

parameters for each of the four elements determined by flameless absorption are given in Table I.

For the determination of Cu, Mn, and Fe, weighed amounts (0.2 to 0.6 g) of the peanut flours and isolates were suspended in 25 mL of deionized water acidified (to 0.5%) with Baker Ultrex nitric acid. The flasks were placed in an ultrasonic bath and agitated for about 10 min to facilitate dispersion of the sample. Eppendorf microliter pipets were used to transfer the suspension to the graphite tube. A small portion of the tip of the pipet was cut off to prevent clogging by solid particles. To further enhance replication, the flasks were thoroughly shaken just prior to removing each sample. With this technique, the coefficient of variation was less than 20% for most determinations.

Because of the extreme sensitivity of the 214-nm Zn line, it was necessary to use the 308-nm line. The sensitivity at this wavelength is about $^1/_{3500}$th of the sensitivity of the 214-nm line.

The flours and isolates were thoroughly mixed after preparation to obtain homogeneity, then were analyzed for zinc directly by weighing 1 to 3 mg of solid into a tared tantalum boat. The Perkin-Elmer solid sampling device was used to position the sample in the furnace. At least five replicate determinations were made on each sample. The coefficient of variation ranged around 20%.

Standards were prepared by appropriate dilution of 1000 ppm standard solutions prepared especially for atomic absorption. A computer program was used to calculate the 90% confidence level on the standard curve for the atomic absorption determinations. This value was incorporated into the calculations for sample standard deviation.

Four elements, K, Ca, Na, and Mg, were determined using an X-ray fluorescence spectrometer (General Electric Model XRD-6) according to standard published techniques (Piccolo et al., 1968). Approximately 200 mg of each of the flours and isolates were pressed into 1-in. diameter disks and analyzed directly. A minimum of two determinations was made on each sample. Replicate analyses gave the following percent deviation for each element: Ca, 0.02%; K, 0.02%, Mg, 0.03%; Na, 0.01%.

National Bureau of Standards orchard leaves were analyzed under the same conditions as the samples as a check on the method.

RESULTS AND DISCUSSION

For the peanut flours and isolates, the amounts of primary metals, Ca, K, Mg, Na, and Fe; plus the essential trace metals Mn, Cu, and Zn, are reported in Tables II and III.

The concentration of Ca in the protein isolates is lower than in the flours. If the concentration is expressed as mg/100 g of protein (multiplying the flour value by 2), the drop in Ca content is even more dramatic. This mineral may be associated with phytic acid which is not removed in the preparation of the flours but which is removed in preparation of the isolates, and this may account for the reduction in Ca content. The Ca content of the flours is approximately twice that reported by Derise et al. (1974) for raw peanuts and almost three times that reported by Galvao et al. (1976). Preparation of flour from whole peanuts, therefore, appears to concentrate the Ca in the flour. Some of this Ca may be unavailable, however, as it may be bound to phytic acid.

The concentration of K in the peanut flours is about twice that reported by both Derise et al. (1974) and Galvao et al. (1976) for raw peanuts. The K content of the isolates is generally about three times that of the raw peanuts. For some unknown reason, however, Starr variety peanuts from Georgia, Virginia, and Oklahoma showed a greatly decreased K content in the isolates compared to the original flours. The K in this cultivar was much more soluble than for the others. This suggests that foods fortified with peanut protein isolates instead of with defatted peanut

Table III. Mineral Element Contents of Peanut Flours and Isolates by Flameless Atomic Absorption

variety	location	form[a]	element, mg/100 g			
			Mn	Cu	Fe	Zn
Florunner	Ga.	F	6.15 ± 0.96[b]	5.16 ± 0.88	10.9 ± 1.9	7.00 ± 1.59
Florunner	Ga.	S	3.12 ± 0.46	14.6 ± 2.5	1.94 ± 1.3	6.79 ± 1.31
Starr	Ga.	F	3.78 ± 0.29	1.01 ± 0.12	5.29 ± 1.47	5.03 ± 0.65
Starr	Ga.	S	2.83 ± 0.12	2.11 ± 0.45	5.44 ± 2.88	3.04 ± 0.58
Florigiant	Ga.	F	6.07 ± 0.62	1.85 ± 0.20	3.39 ± 1.34	5.61 ± 1.12
Florigiant	Ga.	S	3.35 ± 0.66	4.35 ± 0.26	5.62 ± 1.49	5.88 ± 0.65
Starr	Va.	F	3.09 ± 0.46	1.93 ± 0.54	3.82 ± 0.49	7.89 ± 3.18
Starr	Va.	S	3.03 ± 0.61	7.56 ± 1.48	6.72 ± 0.88	18.2 ± 3.12
Florunner	Va.	F	3.69 ± 0.31	1.59 ± 0.18	4.57 ± 0.78	4.66 ± 0.90
Florunner	Va.	S	3.11 ± 0.19	3.33 ± 0.72	3.68 ± 1.12	5.49 ± 1.03
Florigiant	Va.	F	3.52 ± 0.38	1.70 ± 0.17	1.86 ± 0.89	6.05 ± 0.52
Florigiant	Va.	S	2.81 ± 0.46	4.62 ± 0.65	3.94 ± 0.88	6.92 ± 1.70
Starr	Okla.	F	3.84 ± 0.35	1.64 ± 0.27	4.75 ± 1.12	5.22 ± 1.16
Starr	Okla.	S	2.37 ± 0.53	3.83 ± 0.72	4.20 ± 1.46	3.34 ± 0.77
Starr	Tex.	F	3.71 ± 0.57	1.43 ± 0.17	3.35 ± 1.19	6.43 ± 2.10
Starr	Tex.	S	1.64 ± 0.14	4.50 ± 0.76	1.46 ± 1.45	4.42 ± 0.92
NBS orchard leaves, analyzed value			9.16 ± 0.32	1.0 ± 0.3	28.6 ± 5.5	2.2 ± 0.4
NBS orchard leaves, certified value			9.1 ± 0.4	1.2 ± 0.1	30.0 ± 2.0	2.5 ± 0.3

[a] F, flour; S, isolate. [b] 90% confidence limit.

flour would require additional potassium for certain types of diets.

The only two elements in this study which are present in the flours in lower concentration than in the raw peanuts are Mg and Na. The concentration of Na in the flours is much less than the 6 mg/100 g reported for raw peanuts by Derise et al. (1974) or the 8 mg/100 g reported by Galvao et al. (1976). The levels of both metals are also lower in the isolates than in the flours, especially on the basis of mg/100 g of protein. Both Mg and Na may be associated with phytic acid and removed along with it during dialysis. The low concentration of Na indicates that these products could be safely used as food supplements by persons on low Na diets. For diets in which higher levels of Mg, Na, and/or K are recommended, the use of a peanut flour rather than the protein isolate as a supplement would be more desirable.

The concentration of Mn was lower in the isolates than in the flours. Manganese is probably also associated with phytic acid and removed with it during dialysis. The level of Mn in the flours was at least 1.5 times that reported by Derise et al. (1974) or Galvao et al. (1976) for raw peanuts.

The Cu in the peanut flours and isolates is probably associated with protein, since on a mg/100 g of protein basis the amount of Cu is approximately the same. The concentration of Cu in the isolates is generally higher than that reported in the literature for raw peanuts.

Layrisse and Martinez-Torres (1971) claimed that iron from plant foods is absorbed to a lesser degree than that from hemeproteins of animal foods. Absorption of nonheme iron could be increased by feeding it along with animal protein such as beef (Waddell, 1974). Peanuts contain a good portion of the iron in the enzymes, peroxidase and catalase (Ory and Cherry, 1972; Cherry and Ory, 1973) that are solubilized during preparation of protein isolates. This iron, therefore, is not bound by phytate and is retained in the protein isolates. It should have high bioavailability.

The concentration of iron in the peanut flours and isolates is higher than that reported for raw peanuts. The coefficient of variation was relatively high, around 30%. The ground peanuts were extracted in a stainless steel Sorvall Omnimixer and may have been slightly contaminated by iron from the steel. The retention of iron in the isolates after extraction of the protein from the flours does not appear to follow a pattern; however, on a basis of mg/100 g of protein, the concentration of iron in the isolates is generally lower than in the flours.

Freeland and Cousins (1976) analyzed 174 foods, not including peanuts, for their zinc contents and reported that the high levels found in all of the types of nuts sampled indicate that nuts should be considered an important source of dietary Zn. In this study, the level of Zn found in the peanut flours is about the same as that reported for raw peanuts by Galvao et al. (1976) and by Derise et al. (1974). The concentration of Zn in the flours is generally higher than that in the isolates on a mg/100 g of protein basis.

There is no conclusive evidence that variety or growing location affects the mineral contents of the flours prepared from these peanut seeds. Any differences showed may have been due to processing. These results correspond to those reported by Ory and Cherry (1972) on gel electrophoretic protein patterns of Virginia, Spanish, and runner peanuts grown in five areas. In that study, peanut protein patterns were consistent among varieties for all areas except for Spanish peanuts grown in Oklahoma.

Meiners et al. (1976) examined raw and cooked dry legumes for nine mineral elements and concluded that raw legumes are relatively high in Ca, Fe, Mg, P, and K and low in Na. The peanut flours in this study are generally higher in K, Mn, Cu, and Zn than are the raw legumes in Meiner's study, but are lower in Mg and Na. The levels of Ca and Fe are about the same in the peanut flours and the raw legumes.

Bird (1975) projected that plant proteins will replace about 1.07 million tons of meats and other proteins in the United States by 1980. Textured vegetable proteins are now derived from soy, but in the future, some will be made from cottonseed, peanuts, and other oilseeds or mixtures of several plant proteins. A recent study by Conkerton and Ory (1976) of several peanut flours as food supplements showed that they have a number of advantages over soy, including high protein solubility, less flatus-causing sugars, and no raw or beany flavor. The current study confirms that these products would also provide good levels of essential minerals. They can be used to increase the nutritional value of acid beverages such as pineapple juice (Conkerton and Ory, 1976), of bread (Kahn et al., 1978), or as meat extenders (Southeastern Peanut Farmer, 1972).

As far as mineral content is concerned, the Florigiant, Florunner, and Starr varieties examined in this study can be used as food supplements regardless of cultivar type or growing location.

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Hemicellulose Composition of Dietary Fiber of Milled Rice and Rice Bran

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Water- and alkali-soluble hemicelluloses from milled rice and alkali-soluble hemicellulose from the bran were isolated, purified, and characterized. The ratios of arabinose to xylose for the four alkali-soluble rice bran and endosperm hemicelluloses were 1.1:1, 0.9:1, 0.9:1, and 0.8:1, 1.3:1, 1.3:1, 1.8:1, and 1:1; and for the water-soluble hemicelluloses, 4:1, 6:1, 7:1, and 7:1. Amino acid patterns for the proteins associated with hemicelluloses indicate that they are atypical of plant proteins. The water-soluble hemicelluloses contain significant amounts of hydroxyproline. Disc gel electrophoresis of one alkali-soluble rice bran hemicellulose suggests that the proteins are chemically bound to the carbohydrate. The range of crude and neutral detergent fiber contents of rice brans was 9.2 to 21.1% and 29.7 to 44.7%, respectively.

As the first phase of investigations on the role of nonstarch carbohydrates of rice, we are examining the qualitative and quantitative differences between the hemicelluloses of rice from different growing areas. Hemicelluloses, along with cellulose, lignin, and pectin, are major constituents of the cell walls of cereal grains, seeds, fruits, and vegetables and, collectively, they are part of the dietary (food) fiber. Dietary fiber of plant foods, especially cereals, is currently receiving much attention as an essential nutrient that has beneficial effects on hypercholesterolemia and various intestinal disorders (Scala, 1976). All of these nonstarch carbohydrates have a unique stability property; they are relatively unchanged by cooking and they are not readily digested by secretions of the human digestive system when eaten (Scala, 1975). Dietary fiber is the general term given to the plant material that is not digested by human digestive enzymes. It is not the same as crude fiber, and its concentration in foods is always higher than that of the crude fiber content (the insoluble residue after sequential extraction of the material with solvent, dilute acid, and dilute alkali). Analysis of crude fiber content may remove 80% of the hemicellulose and 50–90% of the lignin before the residue is estimated (Van Soest and McQueen, 1973). Thus, crude fiber values listed in proximate analyses are not indicative of the hemicellulose content of foods.

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Unlike other fiber constituents such as pectins, cellulose, or lignins, hemicellulose is not composed of only one or two components, but is a complex material containing several hexoses, pentoses, hexuronic acids, and amino acids with different functional groups that are potentially capable of reacting with other components during cooking and digestion. The composition and structure of wheat-flour hemicellulose (pentosans) have been extensively investigated (Neukom et al., 1967, 1975; Cole, 1967; Medcalf et al., 1968; Fincher et al., 1974). Rice hemicelluloses have received relatively little attention (Matsuo and Nanba, 1958; Gremli and Juliano, 1970; Cartaño and Juliano, 1970; Bevenue and Williams, 1956). All of these investigators found glucose, arabinose, xylose, and galactose in this rice polysaccharide. Mannose was also detected, but only after extraction with 24% KOH (Bevenue and Williams, 1956) or after partial enzymatic removal of the main sugar constituent (Gremli and Juliano, 1970). A proteoglycan (hemicellulose) that contained rhamnose, xylose, arabinose, glucose, galactose, and 17 amino acids was isolated by hot water extraction from rice bran (Yamagishi et al., 1975) and was found to contain *O*-α-L-arabinofuranosylhydroxyproline (Yamagishi et al., 1976).

Wheat bran has received much more attention from nutritionists than has rice, but there are differing opinions