Protein and Amino Acid Compositions of Ten Tropical Fruits by Gas–Liquid Chromatography

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The edible portions of 10 different tropical fruits, namely, tucuma (*Astrocaryum tucuma* Mart.), avocado (*Persea americana* Mill.), mamey sapote (*Pouteria sapota* H. E. Moore and Stearn), longan (*Euphoria longan* Lour.), persimmon (*Diospyros sonorae* Standl.), mango (*Mangifera indica* L.), Cattley guava (*Psidium littorale* Raddi), sapodilla (*Manilkara zapota* L.), carambola (*Averrhoa carambola* L.), and loquat (*Eriobotrya japonica* Lindl.), were analyzed for protein and amino acid composition. The crude protein contents of the fruits ranged from 0.4 to 2.7 g/100 g of fresh edible fruit pulp. Aspartic and glutamic acid were high in all fruits examined, and alanine, glycine, serine, hydroxyproline, and proline contents were relatively high in certain fruits. The amino acid compositions of these tropical fruits were compared with those of more traditional fruits (apple, orange, peach, apricot, and date). The tucuma palm fruit contained 5–10 times the amount of required amino acids in orange or apple.

Accurate determination of the protein content and amino acid composition of food is important in nutritional research to provide a foundation for evaluating protein supplies and developing dietary recommendations. United Nation studies have pointed out that tropical and subtropical regions have the greatest need for programs to uncover indigenous sources of available protein. Considerable research has been conducted on nutrient composition of commercially grown tropical and subtropical fruits, particularly the many species of citrus and the common tropical fruits such as pineapple, banana, mango, and avocado. However, the research has generally not covered protein evaluation, and relatively little has been done on many of the other tropical fruits. Since fruits have been generally considered a low protein food, most chemical analyses on fruits are for proximate composition (e.g., moisture, carbohydrate, fat, crude protein, vitamin, and mineral contents, etc.) or amino acid compositions of specific portions of the fruit (Fernandez-Flores et al., 1970; Vandercook, 1977; Price et al., 1975; Hulme, 1971). A survey of recent publications revealed a paucity of quantitative amino acid data on the many edible tropical fruits (FAO, 1970; Hulme, 1971; Nagy and Shaw, 1980).

Because of this general lack of data on fruit as a possible protein source and the availability of tropical fruits, we undertook to analyze a number of tropical fruits for protein value based on total amino acid compositions. Gas–liquid chromatography (GLC) was used for the amino acid analyses since it has been found to be reliable and less costly or time consuming than ion-exchange methodology and comparable with it in accuracy and precision of quantitation (Gehrke et al., 1968; Nair, 1977; Nagy et al., 1978).

MATERIALS AND METHODS

Samples. Except for the tucuma, which was purchased in Brazil, all the fruits analyzed were grown at the USDA Subtropical Horticultural Research Station, Miami, FL, under similar cultural practices and were randomly selected. The texture, taste, and commercial importance of the 10 fruits and comments from the horticulturist are listed in Table I.

The tucuma, a Brazilian palm fruit, was selected because of its esteemed nutritional value in Brazil (Knight, 1978). Some of the palm fruit has been used commercially in the manufacture of margarine and similar products (Menninger, 1977).

Sample Preparation. The edible portion of the fruits was considered to be the whole fruit minus peel and seeds. Duplicate samples (1–6 fruit in each sample) of the edible portion from fresh (or frozen at −20 °C) fruit were homogenized in a Waring Blendor. Duplicate aliquots of each homogenate were analyzed for nitrogen content by a micro-Kjeldahl procedure and for percent solids (100% less percent moisture) (AOAC, 1965). Amino acids were obtained for analyses by hydrolysis of the homogenate with 6 N HCl; asparagine and glutamine were transformed to their respective acids, and tryptophan was destroyed. The *N*-trifluoroacetyl (*N*-TFA) *n*-butyl esters were prepared (Kaiser et al., 1974) for quantitative separation by GLC.

Reagents. The chemicals used for micro-Kjeldahl analyses were described by Hall et al. (1975). For the acid hydrolysis, reagent grade hydrochloric acid (Fisher Scientific, Inc.) was diluted to 6 N. Other chemicals used in the preparation of the samples for amino acid analyses were previously described (Hall and Nagy, 1979).

Chromatography. Hewlett-Packard Model 5750 and 7610 GC's equipped with flame ionization detectors and an Autolab System IVB Chromatography Data Analyzer were used concurrently for the analyses of the *N*-TFA *n*-butyl esters of the amino acids. Column selection was based on previous studies (Nagy et al., 1978; Hall and Nagy, 1979; Nagy and Hall, 1979). The coated supports were prepared as previously described (Hall and Nagy, 1979) and packed in 183 cm × 0.4 cm i.d. glass columns: 0.75% Silar 9CP (Applied Science) on Gas-Chrom Q, 100/120 mesh, was used in the HP 5750; and a mixed phase, 0.5% OV 210–0.5% OV 17–0.4% OV 7, on the same support was used in the HP 7610. Helium at 60 mL/min was used as carrier for both columns.

The Silar column was programmed from 90 to 190 °C at 6 °C/min after a postinjection hold of 4 min and with an upper limit interval of 18 min. The injection port temperature was 200 °C, and the flame detector was at 260 °C. The mixed OV column was programmed from 90 to 210 °C at 8 °C/min after a postinjection hold of 2 min. The injection port was at 250 °C, and the flame detector

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Table I. Background of the Ten Fruites Tested

horticultural names	texture and taste	commercial importance	comment on cultivar tested
tucuma (Fam. Arecaceae), *Astrocaryum tucuma* Mart.	heavy, starchy consistency and bland flavor; suitable for incorporating in soups or stews and may be used in making confections	no commerical importance in the U.S. or other developed countries; grown in Amazonia and sold in the settlements of the region; often harvested from wild or semiwild stands	usually grown from seed; material examined was bought in a river-front market in Belem, Para, Brazil
avocado (Fam. Lauraceae), *Persea americana* Mill. "Young No. 1"	soft and buttery when fully ripe; flavor rich and nutlike	grown only in home yards because of its thin skin	"Young No. 1" bears small, dark-colored, thin-skinned fruit at the beginning of Florida's avocado season; highly cold tolerant but lacks disease resistance
mamey sapote (Fam. Sapotaceae), *Pouteria sapota* H. E. Moore and Stearn; a synonym is *Calocarpum sapota* (Jacq.) Merrill "Pantin"	somewhat like a moist date, soft but slightly chewy; rich sweet taste, no acidity	minor but growing; frozen puree is imported from the Dominican Republic, and Florida-grown fruit finds ready market among Cuban Americans	"Pantin", a rich, high-quality fruit, is the most commonly grown cultivar in Florida
longan (Fam. Sapindaceae), *Euphoria longan* (Lour.) Steud. "Swann"	gelatinous and slightly chewy, similar to a labrusca grape; flavor very sweet, mild and low in acidity	presently grown only as a dooryard tree in Florida; efforts to develop more regularly productive cultivars are underway; grown commercially in Southeast Asia and has long been important in China for fresh consumption, also dried and tinned	"Swann" (P.I. 277458) is not dependably productive in Florida
sonora persimmon, guayaparin, *Diospyros sonorae* Standl. (Fam. Ebenaceae)	soft, mushy texture with several large, smooth seeds; insipid taste	none recorded	well adapted to South Florida's subtropical climate; makes a small evergreen tree
mango (Fam. Anacardiacae), *Mangifera indica* L. "Tommy Atkins"	firm fleshed and more fibrous than many other varieties; juicy, peachlike, with a mild musky taste	"Tommy Atkins" is the most important commercial cultivar in Florida; with one other cultivar "Keitt", it dominates the market; ~6500 million tons of mangos are shipped from Florida annually, and slightly more (6800 million tons) are imported from Mexico; shipped from Philippines to Japan and the Middle East and from Israel to Europe; grown in many warm countries	"Tommy Atkins" originated in Florida and is disease resistant; it bears a beautiful, bright red fruit that gives it an advantage in the market
yellow Cattley guava Fam. Myrtaceae), *Psidium littorale* Raddi, var. *lucidum* (Deg.) Fosberg	grainy texture from large, hard seeds; subacid to sweet flavor with pleasant light aroma less pungent than that of common guava (*Psidium guajava*); makes excellent jelly and marmalade	very slight as a food crop; sold by Florida and California ornamental nurseries, grown in dooryards in Brazil, southern half of Florida, and warm parts of California	usually grown from seed, and named cultivars are not common; an octoploid ($2n = 88$) that shows little seedling variation; cold resistant
sapodilla (Fam. Sapotaceae), *Manilkara zapota* (L.) Van Royen	soft and yielding; sweet, entirely lacking in acidity; some unimproved cultivars have unpleasant chewy latex (chicle) in the flesh	relatively slight at present (~20 ha) but slowly increasing	"Prolific" is one of the most dependably productive cultivars grown in South Florida
carambola (Fam. Oxalidaceae), *Averrhoa carambola* L. "Tean Ma"	crisp and juicy; "Tean Ma" has a very mild, sweet flavor; others are more acid, and some seedlings are quite sour	minor crop in Florida at present (probably less than 20 ha) but is expanding; experimental shipments to Europe have been successful	"Tean Ma" is a large-fruited cultivar introduced from Taiwan by USDA in 1961 as P.I. 272067; because of its bland flavor (associated with low acid content), it is less popular than "Golden Star" and several others with high flavor
loquat (Fam. Rosaceae), *Eriobotrya japonica* (Thunb.) Lind.	juicy and melting; flavor delightfully sweet and subacid, with a winelike (vinous), fruity aroma	greatest importance in Florida is as an ornamental, small shade tree; also grown on a small scale in California; most important in Japan and Israel where high production per unit of land has been attained	"Christmas" was selected locally (in South Florida) by a private grower; fruit ripens early in season

Table II. Size, Solids, Protein, and Amino Acid Composition of Ten Tropical Fruits

			edible portion					
				crude protein, g/100 g				
fruit	whole fruit wt, g	% edible	% solids[a]	N × 6.25	N × 5.7	total amino acids, mg/100 g	total required amino acids,[b] mg/100 g	% required amino acids
tucuma	20	19	45	2.67	2.44	2545	1181	46.4
mamey sapote	800	82	34	2.12	1.94	1827	535	29.3
avocado	85	57	21	1.61	1.47	1418	666	47.0
longan	6	52	19	1.31	1.19	961	301	31.3
persimmon	20	60	24	0.62	0.57	512	234	45.8
mango	550	69	15	0.42	0.38	428	182	42.6
loquat	14	75	15	0.43	0.39	387	146	37.7
Cattley guava	15	34	17	0.58	0.53	382	154	40.3
sapodilla	200	82	22	0.44	0.40	371	150	40.4
carambola	85	70	10	0.38	0.35	362	149	41.4

[a] 100% − % moisture. [b] Required (combined total of) isoleucine, leucine, lysine, methionine, cysteine, cystine, phenylalanine, tyrosine, threonine, valine, and histidine.

Table III. Required[a] Amino Acid (g/100 g of Total Recovered Amino Acids) Content of Ten Tropical Fruits

fruit	Ile	Leu	Lys	Met	Cys[b]	Phe	Tyr	Thr	Val	His
tucuma	4.9	7.9	5.3	1.3	*1.1*[c]	4.2	*5.7*[c]	5.1	6.0	*4.9*[c]
avocado	5.1	8.9	7.5	2.0	0.3	5.2	3.5	5.3	*7.7*[c]	1.5
mamey sapote	*2.5*[d]	*4.6*[d]	*4.6*[d]	1.0	1.0	*2.9*[d]	3.0	*3.2*[d]	*4.2*[d]	2.3
longan	2.7	5.6	4.8	1.4	0.3	3.1	2.6	3.5	6.0	1.3
persimmon	5.1	9.9	7.5	1.0	0.8	*5.4*[c]	3.9	5.1	7.1	2.3
mango	4.6	7.5	6.6	1.7	0.9	4.4	2.5	4.6	6.8	3.0
Cattley guava	*5.5*[c]	*10.2*[c]	5.8	0.8	*0.2*[d]	3.7	*1.8*[d]	*5.7*[c]	5.3	1.2
sapodilla	4.1	6.6	*9.7*[c]	*0.3*[d]	0.4	3.5	3.9	3.3	4.4	4.2
carambola	4.3	7.8	7.7	*2.1*[c]	0.4	3.7	4.3	4.5	5.1	*0.9*[d]
loquat	4.4	7.1	6.2	1.2	0.3	3.8	2.9	4.0	6.4	1.3

[a] Tryptophan was not determined. [b] Cys equals cysteine and cystine. [c] Highest value. [d] Lowest value.

was at 245 °C. A different program was used for the determination of histidine, namely, 140 to 210 °C at 8 °C/min after a 6-min postinjection hold (Hall and Nagy, 1979).

Calculations of total and individual amino acids (mg/100 g of fruit) were by the Internal Standard Method (Gehrke et al., 1968). Amounts of each amino acid relative to the total recovered amino acids were also calculated and expressed as g/100 g of total recovered amino acids. Duplicate hydrolysates of tucuma, mamey sapote, persimmon, and sapodilla were analyzed by ion exchange at the USDA Russell Research Center, Athens, GA, for comparison.

RESULTS AND DISCUSSION

We found the crude protein, total amino acid content, and "required amino acid content" (which better identifies nutritional value) much higher in one fruit (tucuma) than in any of the others. ["Required amino acids" in the context of this paper include not only the essential amino acids but also cysteine, cystine, tyrosine, and histidine. (Tryptophan is excluded because it decomposed during acid hydrolysis.)] Avocado, mamey sapote, and longan had a higher than average protein nutritional value also, but not comparable with that of tucuma. Most commercially grown fruits contain an average of 0.8 g of crude protein-/100 g of fresh fruit pulp (FAO, 1970). When fruits are found with several times this amount, they gain importance as a potential protein source. This is particularly true for fruits in tropical areas, where protein availability is not sufficient (or is marginal) for growth and/or maintenance of health.

The fruits varied greatly in appearance, size, texture, flavor, and aroma. Their size, edible portion, percent solids, protein content, and summarized amino acid compositions are shown in Table II. We used two factors to calculate crude protein from nitrogen content. One factor, 6.25, has been widely used (Orr and Watt, 1957; FAO, 1970) and is especially recommended in cases where a specific factor has not been determined for the type of food. The other factor, 5.70, is recognized as probably being more realistic for calculating plant proteins used for food and feeds (Tkachuk, 1977). Of course, any factor will be imprecise and imperfect to some extent because of the assumptions that all nitrogen present is protein nitrogen and that all proteins in the particular food have the same nitrogen content. In our study the calculated protein–nitrogen factor (total amino acids recovered/Kjeldahl nitrogen) ranged from 4.6 to 6.4, indicating the 5.7 factor as being more accurate. Mango and tucuma, with calculated values of 6.4 and 6.0, respectively, had the highest amino nitrogen content and Cattley guava and longan, with 4.6, had the least. Values for both crude protein content and quantity of total amino acids indicate that mamey sapote contained about 30% more protein value than avocado, but in terms of required amino acids, avocado contained 20% more than mamey sapote. The limitations of the crude protein and total amino acid data emphasize the need for comprehensive amino acid analyses if fruits are to be more accurately evaluated for protein nutrition. Free amino acids, as well as those obtained from peptides and proteins, should be analyzed.

The gas–liquid chromatographic method used was evaluated by comparison of the resulting data with those obtained by ion-exchange analyses of portions of the same hydrolysate solution on four samples. The greatest variation (5–10%) on particular amino acids was no greater than the variations obtained between samples of the same fruit.

The total amino acid compositions of the fruits (in g/100 g of recovered amino acids for the purpose of comparison) are presented in Table III (the required amino acids) and Table V (nonrequired). Histidine is included as a required

Table IV. Comparison of Required Amino Acid Contents of Ten Tropical Fruits with Those of Five Other Fruits (mg/100 g of Fruit)

fruit	Ile	Leu	Lys	Met	Cys	Phe	Tyr	Thr	Val	His	total req
tucuma	125	201	135	33	28	107	145	130	153	125	1181
avocado	72	126	106	28	4	74	50	75	109	21	666
mamey sapote	46	84	84	18	18	53	55	58	77	42	535
dried date[a]	66	114	81	22	52	74	21	76	93	33	632
longan	26	54	46	13	3	30	25	34	58	12	301
persimmon	26	51	38	5	4	28	20	26	36	12	234
mango	20	32	28	7	4	19	11	20	29	13	182
peach[a]	13	29	30	31	9	18	21	27	40	17	235
orange[a]	23	22	43	12	10	30	17	12	31	12	212
Cattley guava	21	39	22	3	1	14	7	22	20	5	154
sapodilla	15	24	36	1	1	13	14	12	16	16	150
carambola	16	28	28	8	1	13	16	16	18	3	149
loquat	17	27	24	5	1	15	11	15	25	5	146
apricot[a]	14	23	23	4	-[b]	13	10	16	19	13	135
apple[a]	13	23	22	3	5	10	6	14	15	7	118

[a] FAO (1970). [b] Not reported.

Table V. Nonrequired Amino Acid (g/100 g of Total Recovered Amino Acids) Content of Ten Tropical Fruits

fruit	Arg	Ala	Asp	Glu	Gly	Pro	Ser	Hyp
tucuma	4.3	6.1	8.6	10.3	*11.8*[a]	4.2	6.4	1.9
avocado	2.9	7.5	10.9	13.1	6.5	5.1	5.4	1.6
mamey sapote	3.0	6.3	*29.1*[a]	11.8	*3.1*[b]	*3.1*[b]	*12.4*[a]	1.9
longan	3.6	*16.2*[a]	13.0	*21.6*[a]	4.4	4.4	5.0	0.8
persimmon	3.4	7.7	13.9	10.1	6.5	5.7	5.1	1.9
mango	4.6	*15.0*[a]	9.3	13.3	4.9	4.6	4.9	0.8
Cattley guava	3.9	7.5	9.7	*19.8*[a]	7.5	4.6	4.5	2.3
sapodilla	4.6	*3.8*[b]	8.5	10.2	4.5	*9.7*[a]	4.9	*13.4*[a]
carambola	2.1	7.3	10.0	14.8	5.1	5.1	8.2	6.6
loquat	3.7	6.4	12.1	17.2	6.0	*9.7*[a]	6.2	1.0

[a] Extremely high value. [b] Extremely low value.

Table VI. Comparison of Nonrequired Amino Acid Contents of Ten Tropical Fruits with Those of Five Other Fruits (mg/100 g of Fruit)

fruit	Arg	Ala	Asp	Glu	Gly	Pro	Ser	Hyp
tucuma	109	155	219	262	300	107	163	48
avocado	41	106	155	186	92	72	77	23
mamey sapote	55	115	532	216	57	57	227	35
dried date[a]	66	147	201	271	150	159	98	-[b]
longan	35	156	125	208	42	42	48	8
persimmon	17	39	71	52	33	29	26	10
mango	20	64	40	57	21	20	21	3
peach[a]	17	40	92	143	16	27	34	-[b]
orange[a]	52	51	114	99	83	45	23	-[b]
Cattley guava	15	29	37	76	29	18	17	9
sapodilla	17	14	32	38	17	36	18	50
carambola	8	26	36	54	18	18	30	24
loquat	14	25	47	67	23	38	24	4
apricot[a]	10	28	191	48	14	22	23	-[b]
apple[a]	10	17	78	42	14	13	16	-[b]

[a] FAO (1970). [b] Not reported.

amino acid because recent studies indicate that it is essential for the normal maintenance of the adult male (Koppel and Swendseid, 1975), for growth (Rose, 1957), in protein-deficient diets (Sheng, 1974), and in uremic man (Koppel and Swendseid, 1974). Partially fulfilling the need for essential amino acids, the sulfur acids, cysteine and cystine (reported together as Cys), are included because they have a sparing action on methionine; the aromatic amino acid tyrosine is included because it has a sparing action on phenylalanine.

The range of values for required amino acids among the various fruits was generally rather narrow (e.g., Ile 2.5–5.5 mg/100 g of fruit), suggesting a possible general relationship between required amino acids and total amino acids in fruits. More study is needed to validate this point.

Ten tropical fruits were compared with five common commercially grown fruits [data from FAO (1970)] on the basis of mg of amino acid/100 g of fruit (Table IV). In terms of required amino acids, seven tropical fruits were similar to apple, apricot, peach, or orange. Tucuma, however, contained 10 times the required amino acids in apple. Mamey sapote and avocado respectively had 5 and 6 times more required amino acids than apple. The nutritional balance of the amino acids in these fruits is limited by the low quantity of sulfur amino acids. The contribution that 100 g of fruit can make to the required amino acids in the diet is significant. One hundred grams of tucuma would provide 17–26% of the minimum daily requirement (MDR) for the normal adult male of the nonsulfur, required amino acids. The same quantity of avocado and mamey sapote would provide 10–15 and 7–12%, respectively, of the MDR of these amino acids.

The nonrequired amino acids (Table V) except for arginine, which constituted a low percentage of the total, exhibited a wide range of values among the fruits, e.g., Asp 8.5–29.1 g/100 g of recovered amino acids. Generally, with respect to the content of any given amino acid, one or two fruits were much higher (1.5 or more times) than all the others. The surprisingly high levels of aspartic acid in mamey sapote, glycine in tucuma, and hydroxyproline in sapodilla were confirmed by ion-exchange analyses. The very high hydroxyproline content in sapodilla suggests a high level of hydroxyproline-containing proteins (e.g., extensin), which could be present in the cell walls (Lamport and Miller, 1971; Trowell, 1977). This suggestion is supported by the report (Venkataraman and Reithel, 1958) that sapodilla contains oligosaccharides, often associated with such proteins. Overall, glutamic and aspartic acids were most frequently found in larger quantities than the other amino acids. The alanine content was outstanding in mango and longan, as was the proline content of sapodilla and loquat and the serine content of mamey sapote. The quantities (in milligrams) of the nonrequired amino acids supplied by 100 g of fruit are shown in Table VI. The contrast of the highest value (e.g., Asp 532 mg) compared with the range of other values (Asp 32–219 mg) is readily apparent.

CONCLUSION

Certain tropical fruits contain from 10 to 26% of the minimum daily requirement of most essential amino acids per 100-g serving of natural fresh fruit. Tucuma palm fruit, in particular, contains a large quantity of all the required amino acids except the sulfur amino acids (and possibly tryptophan which was not determined).

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Isolation and Identification of the Major Polar Metabolites of Methidathion in Tomatoes

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Tomatoes treated topically with [^{14}C]methidathion equivalent to 10 ppm in the whole fruit were found to produce two major polar metabolites. One was characterized by chromatographic techniques as demonomethyl methidathion. The second metabolite was identified by mass spectrometry as a cysteine conjugate. Confirmation of the postulated structure for the cysteine conjugate was done by cochromatography with a synthesized standard using several thin-layer chromatographic and electrophoretic systems. A method for synthesis of this conjugate is reported. The presence of these metabolites in other crops is discussed.

Methidathion, *S*-[5-methoxy-2-oxo-1,3,4-thiadiazol-3-(2*H*)-yl] *O*,*O*-dimethyl phosphorodithioate, is an organophosphorus insecticide widely used on citrus, tobacco, alfalfa, cotton, sorghum, and several other crops. Its metabolism in higher plants has been investigated by several workers (Bull, 1968; Cassidy et al., 1969; Dupuis et al., 1971).

Demonomethyl methidathion was postulated to be one of the polar metabolites present in cotton by Bull (1968)

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