Dry Bean Tannins: A Review of Nutritional Implications[1]

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ABSTRACT

Tannins are one of several antinutritional factors present in dry beans and are located mainly in the seed coat or testa. The tannin content of dry beans ranges from 0.0 to 2.0% depending on the bean species and color of the seed coat. Many high tannin bean varieties are of lower nutritional quality than low tannin varieties of beans. Naturally occurring food legume tannins are reported to interact with proteins (both enzyme and nonenzyme proteins) to form tannin-protein complexes resulting in inactivation of digestive enzymes and protein insolubility. Both in vitro and in vivo studies indicate that bean tannins decrease protein digestibility, either by inactivating digestive enzymes or by reducing the susceptibility of the substrate proteins after forming complexes with tannins and absorbed ionizable iron. Other deleterious effects of tannins include a lowered feed efficiency and growth depression in experimental animals. The antinutritional activity of bean tannins can be reduced by processing (1 or a combination of 2 or more methods), for example dehulling, soaking, cooking and germination. Genetic selection also may help in breeding varieties low in tannins. Potential chemical treatments such as use of tannin complexing agents are discussed.

INTRODUCTION

Dry beans are a major part of the traditional diet of many countries, notably Asia, Africa and Central and South America. Food legume availability statistics (1) show a per capita daily consumption of 3 to 5 g in Sweden, Argentina, Saudi Arabia and Australia; 50 to 100 g in India, Brazil, Mexico and Japan, and an average of 136.5 g in Burundi. In the U.S. the per capita daily consumption of dry beans is about 16.1 g (2). Nationwide food consumption surveys (3) show that low income groups consume more beans than other socio-economic groups (4). Although food legumes comprise a large number of species, dry beans such as navy, pinto, kidney and Great Northern beans (*Phaseolus vulgaris* L.), bean sprouts and frozen green peas and green bean pods are popular in the U.S. and Europe (3).

Dry beans are good sources of proteins and carbohydrates. However, they also contain several antinutritional and/or toxic factors such as trypsin, chymotrypsin and alpha-amylase inhibitors, phytohemagglutinins, phytates, tannins, etc. In the past, much attention has been given to destruction of antinutritional factors such as trypsin and chymotrypsin inhibitors, phytohemagglutinins and phytates by appropriate processing. Recently dry bean tannins (polyphenols) have received considerable attention largely as a result of their possible influence on the nutritional and aesthetic qualities of foods, biochemical and physiological functions and their pharmacological and toxicological implications. This paper reviews and summarizes recent research on legume tannins and their possible influence on nutritional quality of legumes as human food.

OCCURRENCE AND TANNIN CONTENT

Tannins in dry beans have been determined by various methods and expressed as catechin or tannic acid equivalents. The tannin content of several dry beans is summarized in Table I, which shows a range from 45 mg/100 g in soybeans to 2000 mg/100 g in faba beans. Among dry beans, black gram, faba bean, green gram (mung bean), horse gram, kidney bean, moth bean, peas and pigeon peas have the highest tannin content. It appears that tannin content in beans varies with the color of the seed coat or testa.

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TABLE I

Tannin Content of Food Legumes

Bean	Tannin content (mg/100 g)		Reference
	Whole bean	Cotyledon	
Adzuki bean (*Vigna angularis* L.)	290	–	9
Black gram[a] (*Phaseolus mungo* L.)	540–1197	16–33	77
Chick pea[a] (*Cicer arietinum*)	78–272	16–38	77
Cowpea[a] (*Vigna sinensis* L.)	175–590	28	37
Faba beans[b] (*Vicia faba* L.)	750–2000	740–910	50, 52
Green gram[a] (*Phaseolus aureus* L.)	437–799	21–39	77
Horse gram[b] (*Dolichos biflorus* L.)	1600	–	86
Kidney bean[a] (*Dolichos lablab*)	1024	73	37
Lima bean[b] (*Phaseolus lunatus*)	650–930	–	87
Moth bean[b] (*Phaseolus aconitifolius*)	1300	–	86
Peas[b] (*Pisum sativum* L.)	500–1050	460–560	52
Pigeon pea[a] (*Cajanus cajan*)	380–1710	22–43	77
Soybean[a] (*Glycine max* L.)	45	34	37
U.S. dry beans[a] (*Phaseolus vulgaris* L.)			
Cranberry	76.3	10.0	7
Viva pink	122.1	10.4	7
Pinto	264.7	14.2	7
Light red kidney	152.2	22.2	7
Dark red kidney	105.3	28.7	7
Small red	282.8	19.0	7
Black beauty	33.7	10.8	7
Winged bean[b] (*Psophocarpus tetragonolobus* L.)	158–750	108	76, 88

[a]Tannin content expressed as catechin equivalents.
[b]Tannin content expressed as tannic acid equivalents.

TABLE II

Changes in Polyphenol Content of Winged Bean Seeds During Maturation[a]

Stage of maturity	Polyphenols[b] (%)		
	Sri Lanka	Nigeria	Indonesia
I	3.2	2.6	2.5
II	1.7	2.1	2.0
III	1.5	1.6	1.8
IV	1.4	1.6	1.6
Mature	1.3	1.4	1.4

[a]Compiled from Ref. (13).

[b]Measured as tannic acid equivalents. I = 40 days, II = 50 days, III = 60 days, IV = 70 days, and Mature = 80-85 days after flowering.

Bressani and Elias (5) observed lower amounts of tannins in white than in black, red and bronze colored varieties of *Phaseolus vulgaris* L. A study of tannin content of 29 common bean varieties of *Phaseolus vulgaris* L. using a modified Vanillin-HCl assay (6) concluded that white seeded varieties contained no detectable amounts of tannins, while colored seeded varieties contained large quantities of tannins. Similar observations also were made recently by Deshpande et al. (7) and Deshpande and Cheryan (8) on beans of *Phaseolus vulgaris* L.

Price et al. (9) assayed 10 varieties each of cowpeas, chick peas, pigeon peas and mung beans for tannin content by the Vanillin method. Tannin content ranged from 0.0 to 0.7% for cowpeas and 0.0 to 0.2% in pigeon peas, with essentially no tannin in chick peas or mung beans. However, data of other researchers (Table I) show appreciable amounts of tannins in both chick peas and mung beans. Tannins were assayed by 2 different methods, and quantitative variation may be attributed to the method of assay as well as bean variety. Year, storage, cultivars and growing conditions have been shown to influence concentration of tannins in faba beans (10, 11), suggesting that these factors also should be taken into account when discussing legume tannins.

Tannin content in beans changes during seed maturation. For example, tannin content of winged beans decreases as the seeds mature (Table II). A similar decrease in tannin content was observed during fruit maturation by Goldstein and Swain (12). This decrease in tannin content during maturation may be due to polymerization of existing polyphenolic compounds to high molecular weight insoluble polymers such as lignins (13). Major amounts of bean tannins are located in the seed coat or testa (5, 7, 14), with low or negligible amounts in the cotyledons.

Condensed tannins constitute the major portion of dry bean tannin content. Few studies are reported relative to structures of condensed tannins in legumes. Stickland (90) studied the condensed tannins of peas (*Pisum sativum*). The condensed tannins of peas are found to be of proanthocyanidin (polyhydroxy-flavan-3-ol) type. Martin-Tanguy et al. (15) reported that seed coats of horse beans (*Vicia faba* L.) contain condensed tannins of the proanthocyanadin type. These polymers consist of molecules of flavan-3-ols (catechin and gallocatechin) and flavan-3, 4-diols (leucocyanidin and leucodelphinidin), and are joined together by a carbon-carbon bond between C_4 of one unit and C_6 or C_8 of another. They further reported that these condensed tannins are linear chains, with each chain containing a flavan-3-ol unit at the terminal end. Marquardt et al. (16) purified the tannins (water-extractable, soluble in 90% acetone) in faba bean hulls (testa) and characterized them as condensed tannins. Condensed tannins of faba bean hulls yielded 2 fractions (A and B) on separation with Sephadex LH-20 column. Fraction A contained low molecular weight polyphenolics and B, the major fraction, contained soluble condensed tannins.

Sosulski and Dabrowski (17) recently fractioned the phenolic constituents in the defatted flours and hulls of 10 legume species into free acid, soluble ester and residue components. They hydrolyzed the soluble ester and residue components of flours and hulls with alkali (NaOH) and quantitated the liberated free phenolic acids in the hydrolyzates by capillary gas-liquid chromatography (GLC). The total free phenolic acids (*trans*-ferulic, *trans*-p-coumaric and syringic acids) in legume flours (mung bean, field pea, lentil, faba bean, pigeon bean, navy bean, lupine, lima bean, chick pea and cowpea) ranged from 1.8 mg to 16.3 mg per 100 g of flour. They further detected major amounts of the total free phenolic acids (p-hydroxybenzoic, protocatechuic, syringic, gallic, *trans*-p-coumaric and *trans*-ferulic acids) in the soluble ester component of hulls.

ANTINUTRITIONAL EFFECTS OF TANNINS

Man consumes a number of foods containing considerable amounts of dietary tannins. Common sources of dietary tannins include dry beans, canned and frozen peas, cereal products, leafy and green vegetables and other sources such as coffee, tea, cider and some wines. The intake of dimeric flavans is about 400 mg/day in human diets from a variety of sources in most parts of the world (18, 19). Total dietary tannin intake may be somewhat higher than dimeric flavans. For example, analyses of diets consumed in different regions of India indicated that daily intake of tannin varies from 1500 to 2500 mg (37). Indian diets are composed of several ingredients (rice, wheat, sorghum, dehulled beans, leafy and other green vegetables, roots and tubers, milk, egg, fish, meat, sugar and oil). About 10% of the daily intake of tannins is derived from beans in Indian diets. High bean-based diets may supply higher levels of dietary tannins. The contribution of tannins from dry beans, canned and frozen peas in the U.S. is not known. However, this may depend on the composition of the diet and diet patterns. Certain people may take several folds of dietary tannins in their diet. Daily per capita consumption of beans is 16.1 g in the U.S. If one assumes that the U.S. dry beans and peas contain about 1% tannins, then one would expect about 161 mg tannins from dry beans and peas alone in the American diet.

Antinutritional effects of dry bean tannins have been reported to differ with test animal and avian species (20, 21). Certain types of tannins are reported to be quite toxic to some animal and avian species, but have few or no effects on others. Biological effects of tannins in humans and animals vary considerably (19). Recently, Price and Butler (22) and Deshpande et al. (21) reviewed the deleterious effects of various types of tannins and grouped them into the following categories: depression of food/feed intake; formation of tannin complexes with dietary protein and other food components; inhibition of digestive enzymes; increased excretion of endogenous protein; effect of tannin on the digestive tract, and toxicity of absorbed tannins or their metabolites.

Depression of Food/Feed Intake

The minimum amount of dietary tannins from beans needed to cause a growth depression in humans is not known. This is difficult to predict because of the inherent heterogeneity of bean tannins. However, tannin in the diets of rats (14, 23, 24), chicks (16, 25) and ducklings (15) has

TABLE III

Protein Digestibility of Beans (*Phaseolus vulgaris* L.) as Determined in Adult Human Subjects[a]

Protein source	Protein digestibility (%)	
	Apparent	True[b]
Control (cheese)	76.4	88.2
Beans		
Red Jalpatagua	56.1	68.2
Black Jalpatagua	49.5	61.7
White Ipala	62.7	74.5
Black Ipala	53.7	65.7
White Ipala:Black Ipala (50:50)	57.4	69.4

[a]Compiled from Ref. (33).
[b]Using 13 mg N/kg/day for endogenous nitrogen excretion.

been reported to produce reduction in growth rates, protein utilization and dry matter digestibility. Joslyn and Glick (26) reported that feeding of tannic acid to rats at 5% of the diet resulted in lower weight gains (approximately 50% of the control). Lease and Mitchell (27) found that rats could tolerate up to 5% tannic acid mixed in a diet, but higher levels caused a marked growth depression. Lindgren (28) found a negative correlation between protein digestibility and tannin content of peas and faba beans.

Experiments with chicks have shown that 0.5% tannic acid in the diets results in growth depression, and that the 5% level in the diet leads to high mortality (25). Marquardt et al. (16) reported that chicks fed a diet containing 3.9% of purified condensed tannins from faba beans had markedly reduced feed intake, depressed growth rate, reduced amino acid availability and negative fiber retention as compared to those fed a no tannin control diet. Martin-Tanguy et al. (15) found that high tannin content horse beans depressed egg weights and reduced laying rates of hens. Feeding of tannin-rich faba beans in a longer trial decreased the efficiency of food utilization and increased mortality (29). Several other researchers also have reported that tannins in different cultivars of peas, faba beans and other food legumes were responsible for lower digestion coefficients for crude protein in poultry (1, 11, 30-32).

Hernandez et al. (33) fed red, black and white beans and a 50/50 mixture by weight of black and white beans as a sole source of protein to 15 adult human subjects to study bean protein digestibility. They found digestibility values lowest for black followed by red beans (Table III). The highest value was obtained for white beans, with an intermediate value for the mixture of black and white beans. These investigators suggested that the lower digestibility values for colored beans were due to their tannin content.

Growth depression and protein digestibility effects of bean tannins may be related to their astringent taste, which decreases feed consumption, and their ability to form stable and insoluble complexes with dietary proteins (33).

Formation of Tannin Complexes with Dietary Protein and Other Food Components

Tannins form complexes with proteins, carbohydrates and other polymers in foods as well as with certain metal ions such as iron under suitable conditions of concentration and pH (12, 21, 34-37). The greater tendency of tannins to form complexes with proteins than with carbohydrates and other food polymers (38) is attributed to the strong hydrogen bond affinity of the carboxyl oxygen of the peptide group. Zitko and Rosik (39) reported that one tannin molecule binds 2 or more carboxyl oxygens of the peptide group with possible formation of cross links between the protein chains. The degree of cross linking depends on the number and accessibility of peptide carboxyl groups per protein molecule as well as the relative concentration of the reactant.

TABLE IV

Effect of Tannins on in vitro Trypsin Hydrolysis of the Major Storage Protein Fraction (G_1) of French Beans (*Phaseolus vulgaris* L.)[a]

mg tannin[b]/mg protein	% hydrolysis
0	2.2
0.11	0.9
0.27	0.2
2.75	0.0
11.00	0.0
22.00	0.0

[a]Compiled from Ref. (41).
[b]Oak nut gall tannins were used.

Tannin-protein complexes are reported to be responsible for growth depression, low protein digestibility, decreased amino acid availability and increased fecal nitrogen (20, 21, 35, 40). These complexes may not be dissociated at the physiological pH and thus may be excreted with the feces. The major storage protein (G_1) of the french bean (*Phaseolus vulgaris* L.) (41) has been shown to resist tryptic digestion in vitro (Table IV) when exposed to various concentrations of oak nut gull tannins.

Deshpande and Salunkhe (45) investigated interactions of tannic acid and catechin with legume starches. The formation of tannic acid-starch or catechin-starch complexes has been shown to decrease the in vitro amylolysis of several legume starches and others (45, 91). Cooking of the complexes (tannic acid-starch or catechin-starch) at 95 C for 30 min decreases the association of tannic acid or catechin with starches. Whether these complexes dissociate under normal cooking conditions is not known.

Lease and Mitchell (27) reported a marked decrease in blood hemoglobin in rats fed 5% tannic acid. They proposed that this phenomenon was due to the formation of a tannin-iron complex which reduced the availability of iron. Tannins in food legumes reduce ionizable iron absorption by acting as a natural iron chelating agent. About 50 mg of legume tannin binds with about 1 mg of ionizable iron from food (37). The interference of food tannins in absorption of iron varies with the plant species from which tannins are derived (46, 47). Tannins from various sources (tannic acid, tea, black plum and green banana) at a dose level of 0.5 mg/kg body weight per day decrease iron absorption in normal experimental animals (46). The dosage level at which food legume tannins inhibit iron absorption in humans is not known. However, analysis of diets consumed in different regions in India indicated that the daily intake of tannin varies from 1500 to 2500 mg. This large tannin intake may be responsible for low iron absorption and the prevalent iron deficiency in India (37, 48, 49).

Inhibition of Digestive Enzymes

The inhibition of digestive enzymes by dietary tannins may be expected in view of their affinity to form complexes with proteins. The extent of inhibition of digestive enzymes by tannins may depend on factors such as the amount of dietary protein that could be bound in place of some of the enzymatic protein; formation of tannin-protein complexes prior to ingestion and the extent to which they are broken down in the intestine; relative amounts of various enzymes

TABLE V

In vitro Inhibition of Trypsin, Cellulase and α-Amylase Enzymes by Various Faba Bean and Pea Seed-Coat Extracts[a]

	Inhibition (%)					
	α-Amylase		Trypsin		Cellulase	
	No PVP[b]	PVP	No PVP	PVP	No PVP	PVP
Faba beans						
Triple white	4.1	3.3	6.5	6.4	1.8	2.0
Minden colored	64.9	0.1	51.4	8.3	12.8	7.7
Peas						
Filby white	5.4	4.6	7.2	8.0	1.8	1.7
Minerva colored	54.5	1.4	65.8	8.9	9.9	2.8

[a]Compiled from Ref. (52).

[b]PVP = polyvinylpyrrolidone (a tannin complexing agent).

and the order in which they are encountered in the digestive tract; differing affinities between tannin components and the various enzymes; pH; type and source of tannin, and species and age of the animal (21, 22). The in vitro and in vivo studies have indicated that bean tannins inhibit enzymes such as alpha-amylase, trypsin and cellulase (50–53). Griffiths (52) reported that the water extracts prepared from seed coats of faba beans and peas significantly inhibited the activities of trypsin, alpha-amylase and fungal cellulase in vitro (Table V). Further, they observed that, in all cases enzyme activities could be restored by addition of polyvinylpyrrolidone (PVP), a tannin complexing agent. Addition of PVP to seed coat extracts restored enzyme activity to levels comparable with those found for the white seed coat extracts (Table V). The inhibition of enzymes by tannins is reported to be of non-competitive type (52–55) and is believed to be caused by the non-specific binding of tannins with the enzyme protein. Decreased enzyme activity also may result due to binding of tannins with the substrate and subsequent resistance of the complexed substrate towards hydrolysis (21).

The tannins' source also influences the extent of inhibition of digestive enzymes. For example, Singh (89) reported that polyphenols from pigeon pea were more effective in in vitro inhibition of digestive enzymes such as trypsin and chymotrypsin than those of chick pea. Further, he found that the polyphenolic compounds of cultivars with dark testa color showed more inhibitory activity toward digestive enzymes than those with light testa color in both chick pea and pigeon pea.

Griffiths and Moseley (53) found that the activity of both trypsin and alpha-amylase was significantly reduced in rats consuming diets containing colored faba bean testa compared to rats receiving diets containing testa from a white colored faba bean variety which had no tannins (Table VI).

Increased Excretion of Endogenous Protein

As stated earlier, tannins have a great affinity toward complexing with protein under suitable conditons of concentration and pH (21, 34, 36). These complexes are insoluble at the physiological pH and may not be dissociated. Further, these complexes may be resistant to enzyme hydrolysis and subsequently are excreted. The presence of tannins in the diet causes a decreased nitrogen retention in animals and humans (43). Vohra et al. (25) indicated that dietary tannic acid at the 5% level reduces nitrogen retention and increases excretion of nitrogen in chicks. Reduced nitrogen retention can be improved by adding excess amounts of proteins to the diet to compensate for the protein that is complexed with tannins.

TABLE VI

Effect of Experimental Diets Containing White and Colored Faba Beans on Digestive Enzyme Activity in the Rat Intestine[a,b]

Enzyme	Diet 1	Diet 2	Diet 3
Trypsin	19.7	12.3	18.6
α-Amylase	12.1	4.1	14.0
Lipase	4.7	18.7	4.8

[a]Compiled from Ref. (53).

[b]Diet 1 = control; Diet 2 contained seed-coat from colored faba bean (Dylan variety); Diet 3 contained seed-coat from white colored faba bean (Triple white variety). All three diets contained similar levels of ash (21 g/kg), lipid (42–48 g/kg), soluble carbohydrates (842–868 g/kg) and crude protein (115–117 g/kg). Diet 1 contained total phenolics (7 g/kg), Diet 2 (14 g/kg), and Diet 3 (6 g/kg).

Effect of Tannins on the Digestive Tract

Few researchers have studied the deleterious effects of tannins on the alimentary canal of animals. Vohra et al. (25) reported sloughing off of mucosa in the esophagus, subcutaneous edema and thickening of the crop when chicks were fed 5% tannic acid in the diet. When tannins are present in sufficient amounts, they may cause loss of mucus, epithelial edema, irritation and breakdown of alimentary canal tissue. This may, in turn, facilitate greater tannin absorption, thus increasing its toxicity. Ingestion of higher concentrations of tannins can cause gastrocnteritis and congestion of intestinal walls in rats (56) and hemorrhagic gastroenteritis in rabbits (57). Ingestion of excess tannins in diets sometimes causes excretion of mucoproteins, sialic acid and glucosamine in feces of experimental animals (58).

Toxicity of Absorbed Tannins and/or Their Metabolites

Published data relating absorption of tannins through the normal gastrointestinal tissues of animals and toxic effects of this absorption are conflicting. Direct absorption of tannins in healthy animals seems unlikely, probably due to membrane barriers and affinity for complexation. However, chronic ingestion of large amounts of tannin can damage the gastrointestinal surface. Under these conditions, tannins might be absorbed, producing possible harmful effects.

The acute toxicity of orally given tannins is low, but increases greatly when tannins are administered parenterally. The LD-50 values for mice, rats and rabbits after a single large dose of tannic acid given orally ranges from 2.25 to 6.00 g/kg body weight (59). Rectal toxicity of tannic acid is about twice its oral toxicity (56). The LD-50 values for subcutaneous administration of condensed tannins from

TABLE VII

Percent Reduction in Tannin Content of Food Legumes on Dehulling

Beans	Reduction (%)	Reference
Black gram (*Phaseolus mungo* L.)	96.1–98.2	77
Chick pea (*Cicer arietinum*)	74.5–92.6	37, 77
Cowpea (*Vigna sinensis* L.)	84.0	37
Faba beans (*Vicia faba* L.)	53.8	50, 52
Green gram (*Phaseolus aureus* L.)	92.6–97.4	37, 77
Kidney bean (*Dolichos lablab*)	92.9	37
Peas (*Pisum sativum* L.)	46.7	52
Pigeon pea (*Cajanus cajan*)	94.2–98.0	37, 77
Soybean (*Glycine max* L.)	24.4	37
U.S. dry beans (*Phaseolus vulgaris* L.)	68.0–94.6	7
Winged beans (*Psophocarpus tetragonolobus* L.)	31.6	76

different sources (grapes and hawthorn) are reported to be 70–300 mg/kg body weight of the animal (60, 61). Most of the toxicity studies in experimental animals are conducted using commercially available tannins or tannic acid samples. It is difficult to judge whether tannins from food legumes will have similar toxicities in animals. In a limited study with sheep, Edwards et al. (63) found no evidence of toxicity after feeding 62% faba bean hulls for 28 days. No known toxicities in humans have been reported due to ingestion of excessive amounts of bean tannins.

The liver and kidneys in chicks suffer severe damage from feeding of 2–3% tannic acid (19, 25). At cellular and biochemical levels, injection of tannic acid at 700 mg/kg can cause liver fibrosis and necrosis, polyribosome disegregation, and inhibition of microsomal enzymes as well as synthesis of nucleic acid and protein (19, 63–65).

The monomeric units of hydrolyzable condensed bean tannins may not produce toxic effects of pure commercial tannins, since they do not have protein precipitating properties. However, the low molecular weight degradation products of tannins may be easily absorbed across the membrane and thus may be more toxic than the monomeric tannin units. Detailed descriptions of absorption of various hydrolysis products of tannins, and of the general toxicity of several phenolic compounds, are presented in 2 reviews (19, 59). Tannins are reported to cause tumors in experimental animals when applied to burns or injected subcutaneously (66, 67). Some of the tannins and tannic acids have been listed as tentative carcinogens of category I under the generic carcinogen policy of OSHA (68). According to Singleton (19), carcinogenicity of tannins may involve irritation and cellular damage resulting (over a prolonged period) in a high malignancy rate, instead of producing a true deoxyribonucleic acid (DNA) mutagenic carcinogenesis.

Data on the involvement of tannins in carcinogenesis is sketchy. However, chronic ingestion of high amounts of tannins in the diet may increase the risk of tumerogenic disease. Morton (69, 70) suggested that consumption of plant tannins is a possible factor in the incidence of esophageal cancer in many areas of the world. The minimum amount of dietary tannin needed to elicit a negative growth response has not been established. Further, the effect of dietary tannins on humans is unknown, although epidemiological considerations have led to suggest a correlation between condensed tannins and esophageal cancer (71). It is unlikely that condensed tannins would be hydrolyzed in the gut. In fact, prolonged contact of catechin, a component of condensed tannin, with gastric juice causes some polymerization of the compound (72).

REMOVAL OF TANNINS

Several processing methods and chemical treatments have been tried to eliminate tannins from dry beans. These include physical removal of tannins by milling and separating hulls or dehulling; soaking; cooking; germination; plant breeding; addition of agents that complex dietary tannins; addition of agents that aid in metabolic detoxification of tannins, and chemical treatment of food/feed.

Physical Removal of Tannins by Milling and Separating Hulls

Since tannins are located mainly in the testa or seed coats of dry beans, the physical removal of seed coats by either dehulling or milling and separating hulls may decrease the tannin content in beans and improve their nutritional quality (7, 17, 20). Eggum (73) reported that dehulling of faba beans improved nutritional quality. Significant reductions in tannin content of dry beans by removal of seed coats by dehulling have been reported recently (Table VII). Dehulling eliminates 68–99% of tannins in beans (except winged beans, soybeans, peas and faba beans). Small amounts of tannins have been removed by dehulling of winged beans, soybeans, peas and faba beans. Dehulling improves in vitro protein digestibility (7) and ionizable iron absorption (37). Mechanical dehulling of seeds also may result in substantial losses of protein and other nutrients which may partially offset the beneficial effects of tannin removal by dehulling.

Soaking

Soaking of beans before cooking is a common practice in developing countries, and is used to soften the texture and hasten the cooking process. Reduction in tannin content of several beans by soaking in different solutions was reported by Sathe and Salunkhe (74) and Deshpande and Cheryan (8). Pinto beans, with the highest tannin content, show the greatest reduction in tannin content after soaking (Table VIII), whereas cranberry beans, which had the lowest tannin content, lost fewer tannins during soaking. Leaching of bean tannins increases with the time of soaking in distilled water (Table VIII). It is also possible that at least some tannins may diffuse into the cotyledon endosperm and bind with the proteins during soaking. When tannins are bound to proteins, they usually are not detected by routine methods (43, 75). Data of Deshpande and Cheryan (8) indicate that soaking beans in sodium bicarbonate or mixed salt solutions more effectively removes tannins from dry beans than does soaking in water. Soaking of beans in sodium bicarbonate and mixed salt solutions reduces their cooking time. Sathe and Salunkhe (74) similarly reported that soaking of winged beans in dilute alkali (2% potassium hydroxide) effectively removes tannins (87.3% and 82.2%, respectively) from Chimbu and HF-10 varieties (Table IX). However, de Lumen and Salamat (76)

TABLE VIII

Effect of Soaking Tannins of Dry Beans (*Phaseolus vulgaris* L.)[a,b]

Treatment	Pinto beans		Cranberry		Viva Pink	
	Tannins (mg/100 g)	Reduction (%)	Tannins (mg/100 g)	Reduction (%)	Tannins (mg/100 g)	Reduction (%)
Raw beans	264.7	–	76.3	–	122.1	–
Soaked beans						
Distilled water						
6 hr	208.6	21.2	67.0	12.2	100.0	18.1
12 hr	96.1	63.7	57.0	25.3	80.0	34.5
18 hr	69.9	73.6	51.0	33.2	73.0	40.2
2% sodium bicarbonate (w/v)						
12 hr	24.1	90.9	25.0	67.2	27.0	77.9
MSS[c]						
12 hr	18.0	93.2	20.0	73.8	20.0	83.6

[a]Compiled from Ref. (8).

[b]Tannin content was measured as catechin equivalents, all cases, soaking water was discarded.

[c]MSS = Mixed salt solution (2.5% sodium chloride, 1% sodium tripolyphosphate, 1.5% sodium bicarbonate and 0.5% sodium carbonate, all w/v in distilled water).

TABLE IX

Effect of Soaking on Winged Bean Tannins[a]

Treatment	Winged bean varieties			
	Chimbu		HF-10	
	Tannins[b] (mg/g)	Reduction (%)	Tannins[b] (mg/g)	Reduction (%)
Raw beans	51.3	–	40.9	–
Distilled water (24 hr)	16.6	67.6	17.4	57.5
2% sodium hydroxide (24 hr)	6.8	86.7	13.9	66.0
2% potassium hydroxide (24 hr)	6.5	87.3	7.3	82.2

In all cases, beans were soaked for 24 hr in different soaking solutions and the soaked water was discarded.

[a]Compiled from Ref. (74).

[b]Expressed as phloroglucinol equivalents.

observed a reduction of 65% of tannins in Chimbu variety on soaking in sodium hydroxide for six hr at room temperature. The greater removal of tannins obtained by Sathe and Salunkhe (74) may be due in part to the longer soaking time (24 hr).

Cooking

Cooking is a common process used for softening beans. Cooking and discarding of the cook-water results in about 37.5 to 77.0% decrease in tannin content of beans (Table X). Several authors suggest that the apparent decrease in tannins during cooking is most likely not due to an actual decrease in tannins but to a change in their solubility or chemical reactivity. Thus the observed decrease in tannin content of beans during cooking may be due to binding of tannins with other organic substances and proteins, or from alterations in the chemical structure of tannins that cannot be determined by available chemical methods.

Bressani and coworkers (5, 24, 33, 43, 44) at the Institute of Nutrition of Central America and Panama (INCAP), studied the partition of polyphenols in black, white and red beans during cooking. About 60.4, 66.7 and 37.4% of total polyphenols of the raw beans remained in black, white and red colored beans respectively upon cooking (Table XI). The cooking waters contained less than 20% of the total polyphenols. If no destruction of tannins occurs during cooking, it may be assumed that 20.5, 17.8 and 50.9% of the total polyphenols became bound in black, white and red beans respectively. Once the tannins are bound to amino groups of the protein or other compounds

TABLE X

Effect of Cooking on Tannin Content of Whole Dry Beans

Beans	Tannin content (mg/100 g)		Reduction (%)	Reference
	Raw	Cooked		
Black gram	836	256	69.4	77
Chick pea	165	38	77.0	77
Green gram	612	172	71.9	77
Pigeon pea	1141	475	58.4	77
Horse gram	1600	1000	37.5	86
Moth bean	1300	650	50.0	86
Winged bean	1580	620	60.8	76

they cannot be extracted and measured by present analytical methods due to insolubility in solvents normally used. It is also possible that the solids in the cooking water may have higher levels of bound tannins than the cotyledons or whole beans (5).

Bressani et al. (43) hypothesized that part of the polyphenolic compounds remain free and part become bound to other organic components and proteins in beans on cooking. The bound polyphenolics may make the proteins less susceptible to enzymatic hydrolysis in the digestive tract, increasing fecal nitrogen output and thus decreasing protein digestibility. Binding of tannins to lysine of bean proteins may decrease lysine availability. On the otherhand, free polyphenolics may influence protein digestibility indirectly by inhibiting the digestive enzymes. If free polyphenolics

TABLE XI

Distribution of Polyphenols Expressed as Tannic Acid (g/500 g bean) During Cooking of *Phaseolus vulgaris* L. Beans[a]

	Bean color		
	Black	White	Red
Raw beans	4.50 (100.0)[b]	1.80 (100.0)	7.35 (100.0)
Cooked beans	2.72 (60.4)	1.20 (66.7)	2.75 (37.4)
Cooking water	0.86 (19.1)	0.28 (15.5)	0.86 (11.7)
Loss or bound (?)	0.92 (20.5)	0.32 (17.8)	3.74 (50.9)

Experimental conditions: Bean to water ratio was 1:3, cooked for 4 hr at atmospheric pressure or 30 min. under 15 psi.

[a]Compiled from Ref. (43).

[b]Percentage distribution of polyphenols.

TABLE XII

Effect of Germination on Tannin Content of Dry Beans[a]

	Pigeon pea		Chick pea		Green gram		Black gram	
Germination	Tannins (mg/100 g)	Reduction (%)	Tannins (mg/100 g)	Reduction (%)	Tannins (mg/100 g)	Reduction (%)	Tannins (mg/100 g)	Reduction (%)
Ungerminated, raw beans	1141	–	165	–	612	–	836	–
Germinated								
0 hr	595	48	77	53	439	28	649	22
24 hr	544	52	68	59	328	46	534	36
48 hr	464	59	59	64	292	52	390	53

[a]Compiled from Ref. (77).

[b]Beans were soaked in water for 15 hr at room temperature prior to germination. Soak water was discarded.

are absorbed, they usually are excreted as sulfate derivatives, wherein methionine is involved. This results in a decrease of protein quality. Bressani et al. (43) suggested that additional studies should be done to validate their hypothesis about the fate of polyphenolic compounds in beans on cooking.

Germination

Germination reduces or eliminates several antinutritional factors from beans. As a result of overnight soaking in water and subsequent germination for 48 hr, more than 50% of tannins are lost in pigeon pea, chick pea, green gram and black gram (Table XII). Loss of tannins in beans during germination may be attributable to the presence of polyphenol oxidase and enzymatic hydrolysis (77). Some loss of tannins during germination may also be expected from leaching of tannins into the water. Germination increases the ionizable iron absorption in food legumes (37).

Plant Breeding

The presence of tannins and other color pigments in the seed coat or testa of dry beans is genetically controlled (6, 14). Ma and Bliss (6) reported that beans with colored seed coats and low tannin contents can be produced through selection and hybridization. They further reported that the low tannin genes are dominant in beans. It remains to be seen whether reducing the tannin content in seeds with colored seed coats alters other desirable traits such as pest resistance and prevention of pre-harvest germination of seeds. Varieties of *Phaseolus vulgaris* L. beans with colored seed coats usually have a greater disease resistance than white colored beans (78). The colored beans are preferred by most Latin American populations over white beans (5). Whether acceptability of beans is based on color of the seed coat or low tannin content is not known. It may be important from the consumer viewpoint to determine whether polyphenolic compounds are related to acceptability of common beans before initiating genetic selection studies to eliminate them.

Addition of Agents that Complex Tannins

Several chemicals (iron, caffeine, Tween-80, polyvinylpyrrolidone and polyethylene glycol) are reported to complex or interact with tannins (16, 57, 79). These chemicals form complexes with tannins by interacting with their active hydroxyl groups. When used as supplements to diets, these chemicals may prevent formation of tannin-protein complexes or liberate proteins from the complexes. Marquardt et al. (16) found that adding tannin-complexing compounds to bean diets eliminates the growth depressing effect of faba bean tannins. Addition of polyethylene glycol (PEG-4000) at 0.1 g/g protein to high tannin field bean diets results in improved nitrogen digestibility in chicks (80).

Addition of Agents that Aid in Metabolic Detoxification of Tannins

Methionine and chlorine both play a special role in detoxification of tannins in experimental animals (21, 22). Both methionine and choline react with tannins and tannin by-products to form monomethyl ethers. This may result in depletion of the methyl donors, methionine and choline, in the body. Several studies indicate that supplementing tannin-rich diets with methionine and/or choline can counteract the antinutritional effects of condensed or hydrolyzed tannins and improve nutritional quality (25, 81). Recently, Bressani et al. (24) found that addition of methionine to bean diets improved protein quality of the

diets for rats. They suggested that methionine played a key role in metabolic detoxification of bean tannins in rats. Methionine is the first limiting amino acid of several legume proteins. Consumption of high tannin legumes, particularly in areas where they form a substantial part of the diet, might create additional nutritional problems (methionine and choline deficiency) in these populations.

Chemical Treatment of Food/Feed

Treatment of beans and cereals with chemicals (dilute alkali, ammonia, hydrogen peroxide, formaldehyde, ferrous sulfate or ferric chloride) apparently reduces assayable tannin and improves the nutritional quality (74, 82-84). Such treatments may have many advantages over dietary additives, which must act in vivo to be effective. Price et al. (84) reported that moist alkaline conditions detoxify tannins in sorghum. However, the mechanism of tannin detoxification under alkaline conditions is not known. When treated with chemicals, tannins may become altered in some manner so as to become nutritionally unreactive, perhaps by forming phobaphenes (85). Under alkaline conditions, the hydrolyzed tannins may become permanently bound to some components, especially proteins in the seeds, and render these components insoluble and nutritionally inert.

Research Needs

Needed areas of research (43) on dry bean tannins include (i) identification of tannin types in common beans of different color; (ii) fate of tannins in beans during cooking and other processing; (iii) study of protein-binding and enzyme inactivation properties of tannins from different bean cultivars; (iv) identification of possible sites of chemical reactions; (v) improved experimental models and analyses to establish relationships between tannins and protein digestibility, and protein quality in beans; (vi) mechanisms of detoxification of bean tannins, and (vii) development of simpler processing for improving the nutritional quality of high tannin bean cultivars.

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⁂Metathesis of Methyl Oleate with a Homogeneous and a Heterogeneous Catalyst

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ABSTRACT

The cometathesis reaction of methyl oleate (MO) with unsaturated dicarboxylic acid esters has been studied using either a homogeneous catalyst system (WCl_6-Me_4Sn) or a heterogeneous catalyst system (Re_2O_3-Al_2O_3-Me_4Sn). In the presence of the homogeneous catalyst, dimethyl-3-hexenedioate (DMHD) reacted with MO to give cometathesis products in 47% yield with a distribution of products that agreed with the theoretical equilibrium composition. When dipropyl-4-octenedioate (DPOD) was used, however, the yield of cometathesis products was less than 1%. The lower reactivity of DPOD might be due to the formation of a stable complex of DPOD with the catalyst. The cometathesis reaction of MO and DMHD was also catalyzed by the heterogeneous catalyst. However, the reaction rate decreased significantly and the distribution of products did not attain the theoretical. Similar results were obtained in the cometathesis reaction of MO and DPOD catalyzed by the heterogeneous catalyst. These results suggest that MO and DMHD are preferentially adsorbed onto the surface of this catalyst according to their polarity, and that the molar ratio of MO and DMHD at the catalytic site was different from that in the reaction medium.

INTRODUCTION

The first study of the metathesis reaction of functionally substituted alkenes catalyzed by a homogeneous catalyst was reported by Van Dam et al. (1). The self-metathesis reaction of esters having a double bond in the ω position catalyzed by a homogeneous catalyst subsequently were reported by Nakamura et al. (4) and Baker et al. (5). The self-metathesis reaction of methyl oleate catalyzed by a homogeneous catalyst (WCl_6-cocatalyst) was studied in detail by Ichikawa and Fukuzumi (6). The latter authors reported the optimum conditions for the self-metathesis reaction as well as the cometathesis reaction of methyl oleate with 1-decene.

On the other hand, the first study concerning the metathesis reaction of alkenes bearing a functional group catalyzed by a heterogeneous catalyst was reported by Verkuijlen et al. (7). This author studied the self-metathesis reaction of methyl-4-pentenoate using a Re_2O_7-Al_2O_3-Me_4Sn system. Mol et al. reported the self-metathesis reaction of various oxygen-containing alkenes (8) and the cometathesis reaction of methyl oleate with ethylene (9), all catalyzed by the Re_2O_7-Al_2O_3-Me_4Sn catalyst system. In this latter report, the catalytic activity of the homogeneous catalyst (WCl_6-Me_4Sn) and the heterogeneous catalyst were compared.

Only a limited number of studies have been reported on the metathesis reaction of alkenes bearing functional groups. Accordingly, little is known about the scope of the cometathesis reaction of functionally substituted alkenes. Moreover, alkenes which were studied in the cometathesis reaction of methyl oleate were alkenes having no other functional group; e.g., ethylene, 3-hexene, 1-decene and cyclododecene (10). The present study was undertaken to investigate the cometathesis reaction of methyl oleate with unsaturated dicarboxylic acid esters catalyzed by both a homogeneous and a heterogeneous catalyst system.

EXPERIMENTAL

Materials

Methyl oleate was obtained from Applied Science Laboratories (State College, Pennsylvania). Its purity was <99.5% as determined by GLC. WCl_6 was purchased from Strem Chemicals, Inc. (Newburyport, Massachusetts). Tetramethyl tin (Me_4Sn), 4-pentenoic acid, and Re_2O_7 were obtained from Alfa Products (Danvers, Massachusetts). γ-Al_2O_3 (surface area 200 m^2/g) was obtained from Nikki Kagaku, Nippon Oil and Fats Company (Tokyo, Japan). 3-Hexenedioic acid and 10-undecenoic acid were purchased from Fluka Chemical Corporation (Hauppauge, New York) and Eastman Organic Chemicals (New York, New York), respectively. All solvents used were distilled and dried over 4A molecular sieve prior to use.

Methods

Gas liquid chromatography (GLC) was conducted with a Perkin-Elmer model Sigma 3 chromatograph equipped with dual flame ionization detectors. Separations were obtained on a 15 m methyl silicone fluid capillary column (OV-101, Hewlett Packard). A Perkin-Elmer model 720B infrared spectrophotometer was used for IR analysis. Mass spectral

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