Aminopolysaccharides -Their Potential as Dietary Fiber

IVAN FURDA
General Mills, Inc., Minneapolis, MN 55427

Aminopolysaccharides could serve as a new source of dietary fiber having special physiological and in vitro functional properties. The fact that they are of animal and microbial origin and currently not approved for use in foods may be reasons why they have not been considered within the context of dietary fiber. Chitin and chitosan, two major readily available aminopolysaccharides are described in terms of their functional properties in foods, and in their possible role as potential pharmaceutical or food additives. Special attention is paid to their physiological effects in rats. The interaction of chitin and chitosan with lipids and cholesterol, and their effect on lipid absorption suggest that some aminopolysaccharides show strong binding activity towards specific lipids. This activity seems to be a function of the density of positive charge in the aminopolysaccharide molecule where electrostatic forces between lipids and aminopolysaccharides play a greater role than hydrophobic interactions. Since aminopolysaccharides are nondigestible and some reduce lipid absorption in rats. they could be considered as ingredients having "negative" calorie value. The hypocholest-erolemic activity of chitosan and its side effects are compared with currently available hypocholesterolemic agents such as cholest-ramine.

The widely accepted definition of dietary fiber as proposed by Trowell (1) refers to "plant polysaccharides and lignin which are resistant to hydrolysis by digestive enzymes of man" as the sole constituents of dietary fiber. Being limited to the plant polymers only, this definition does not include undigestible polysaccharides from other sources such as those of animal origin, or those which are prepared synthetically. There are several food-approved cellulose derivatives and synthetic gums, and recently polydextrose which "are resistant to hydrolysis by digestive enzymes of man" and therefore, they should be considered dietary fiber as well. Animal aminopolysaccharides which are part of the traditional diet of the Eskimos offer another example (2).

Godding (2) spelled out the limitations of Trowell's definition and proposed a modified definition of so called "edible fiber", which consists of "polysaccharides, related polymers and lignin, which are resistant to hydrolysis by the digestive enzymes of man". It seems logical that all non-digestible edible polymers, regardless of their origin, should be considered dietary or edible fiber because of two common denominators-their polymeric nature and their resistance to hydrolysis by the digestive enzymes of man.

General Properties

The common natural aminopolysaccharides include chitin, chitosan, keratin sulphate, hyaluronic acid, chondroitin and dermatan sulphates, heparin and blood group substances. While chitin and chitosan contain hydroxyl, amino and acetyl groups, the others contain also carboxyl and sulphate groups. In this paper, attention is paid only to chitin and chitosan. Chitin is a cellulose like polymer which is present in fungal cell walls and exoskeletons of arthropods such as insects,

crabs, shrimps, lobsters and others. Chemically, chitin and chitosan are polyglucosamines which are differentiated only by the extent of acetylation of amino groups as shown in Figure 1. Although there is no clear distinction between chitin and chitosan, it is generally accepted that chitin is extensively acetylated, while chitosan is virtually deacetylated. The typical chitins have usually 70 - 95% degree of acetylation (DA) which corresponds to 15 - 20.7% acetyl content while chitosans commonly have 15 - 25% DA corresponding to 3.2 - 5.3 % acetyl content (3). The degree of acetylation is probably the most important parameter in these polysaccharides and it greatly determines their physiological and in vitro functional properties.

Another important parameter is the molecular weight (MW) and its associated viscosity. The average MW of some chitins can exceed 10^6. Chitosan, since it is prepared from chitin by alkaline deacetylation has a lower number average MW ranging usually between 1x10 - 3x1 0^5. Chitosan displays a wide range of viscosities in diluted acid media which depend mainly on its MW (3). The relative viscosity of high viscosity chitosans is comparable with the viscosity of guar or tragacanth gums. The viscosity of chitosan likely plays an important role in its physiological properties later discussed. Only chemically treated (acid hydrolyzed) chitin forms viscous solutions (4).

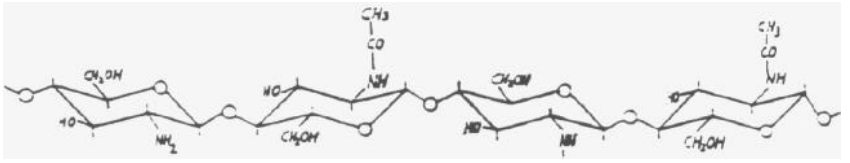
While chitin is insoluble in common solvents (is soluble in concentrated mineral and formic acids and some special solvents), chitosan is soluble in diluted mineral and organic acids (3). Chitosan is not soluble at pH > 6.0 and it functions only in acid systems, which is relevant to its food applicability. Due to the high density of the positive charges chitosan behaves in aqueous acid solutions as a polycationic molecule. This behavior is not typical for chitin because of its high degree of acetylation. Chitosan in the polycationic form binds various anions forming salts or complexes with them. It can be considered a weak anion exchange resin. Chitosan is a strong base toward hydrochloric acid, since the primary amino groups with pK_a 6.3, easily form quaternary nitrogen salts at low pH. At high pH, however, the amino groups of chitosan are weak bases and therefore do not interact with anions and do not dissociate neutral salts.

Potential Applications in Foods

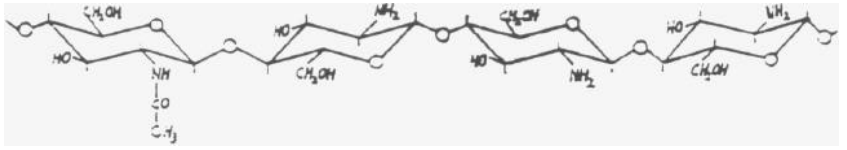
Chitin and chitosan have been recommended as potential feed and food additives because of their useful functional properties. Though officially not approved for use in foods in the U.S., some aminopolysaccharides are part of the traditional diet of Eskimos as well as being present in different Oriental foods such as tempeh, sufu and even aged beef (51. In the nonpurified form, chitin is present in oyster shell powder which is used in animal feed as a source of calcium. Glucosamine, the monomeric unit of chitosan is used extensively in oral pharmaceutical preparations.

Microcrystalline chitin produced by controlled acid hydrolysis may be suitable for use as food thickener and stabilizer (4). The viscosity and emulsion stability of microcrystalline chitin is 10 to 20 times higher than that of crystalline cellulose making it suitable for applications in mayonnaise, peanut butter and other emulsion-type foods (6). Addition of microcrystalline chitin to white and protein fortified breads has been shown to increase specific loaf volume (7).

Chitosan due to its high viscosity in systems of pH < 5.5 can function as thickener, stabilizer or dispersing agent (6). Other applications include gel and film formation (8.9), encapsulation and inclusion in packaging materials (10). Bough



Chitin



Chitosan

Figure I. Chemical structure of chitin and chitosan.

(11) recommended chitosan as a coagulating agent for food processing wastes with its subsequent utilization as animal feed. Recently, Rha and Sanchez (12) prepared and described chitosan globules which simulate the cellular texture of cooked rice and may have other specific texture applications in foods.

Physiological Activity

Chitin and chitosan are believed to be of low toxicity. According to Arai (13) the ID,, of chitosan in laboratory mice is 16 ga/kg of body weight. This is similar to that of salt or sugar. In an eight weeks feeding study (14), it has been suggested that chitosan is safe in rats up to 10% in the diet. At 15% level, enlargement of liver and kidneys with a few other changes have been observed. While chitin is believed to be virtually inert in the gastrointestinal tract of mammals, chitosan has been recently associated with strong hypocholesterolemic activity in rats.

Sugano et al (15), compared chitosan, cholestyramine, cellulose and different brown algae at 5% level in rat diets containing cholesterol. Besides showing lowest weight gain and highest fecal weight, rats fed chitosan also had the lowest plasma cholesterol and showed its greatest excretion. The excretion of bile acids was only slightly enhanced by chitosan as compared to cholestyramine. The results of twenty days feeding experiment are shown in Table I. Of particular interest was the observation that chitosan caused repression of microbial transformation of cholesterol to coprostanol. Cholestryamine, on the other hand, was more effective in reducing liver cholesterol.

Kobayaski et *a/* (16), compared the effectiveness of chitosan with konjac flour and two hypocholesterolemic drugs. Their experiment included one week feeding of cholesterol-containing diet to rats with 4% level of test materials. They observed

that chitosan caused the greatest depression of serum cholesterol level and was superior to konjac flour used at the same level and to moristerol and benikol used at 0.5% and 0.8% levels respectively. While konjac flour and benikol caused severe diarrhea, chitosan did not affect the feces.

Nagyvary et al (17), studied high viscosity (4,000 c.p.) chitosan in relation with cellulose, citrus pectin (9% / CH_30) and A1 salt of pectin at 4% level in rat diet containing cholesterol. The feeding period lasted four weeks. Their observations are summarized in Table II. The level of serum cholesterol in chitosan fed group was approximately 44% lower than in cellulose fed group, 22% lower than in pectin group and about 16% lower than in Al-Pectin fed group. The liver cholesterol was about 60% lower in chitosan-fed group than in the three other groups. There was also a pronounced hypolipidemic effect of chitosan on serum and liver as compared to the other fibers. What seems to be noticeable is the fact that both cholesterol and triglycerides were lowered even more dramatically in liver than in serum.

Table I

PLASMA AND LIVER LIPID CONCENTRATIONS AND FECAL OUTPUT OF NEUTRAL STEROLS*

DIETARY REGIMENS 5%	PLASMA LIPIDS (MG/DL) CHOLEST	TRIGLIC	LIVER LIPIDS (MG/G) CHOLEST	TRIGLIC
CELLULOSE	162 +/- 11 7'	110 +/- 06'	33.3 +/- 2.6'	42.2 +/- 1.7'
CHOLESTYRAMIN	107 +/- 7[a]	146 +/- 13'	5.8 +/- 0.7[b]	24.3 +/- 1.8b
CHITOSAN	94 +/- 1 2	123 +/ 9.	11 +/- 1.7c	30.3 +/- 2.S[b]
UMITORANOO	143 +/- 16'	125 +/- 7'	36.0 +/- 1.9'	49.5 +/- 3.0'

DIETARY REGIMENS	CHOLESTEROL EXCRETED (MG/DAY)	COMPOSITION OF FECAL STEROLS (% OF TOTAL) COPRO	CHOLESTEROL	PHYTO
CELLULOSE	45.3 +/- 2.2[a]	28.6 +/- 3.2'	68.4 +/- 3.5	3.0 +/- 0.8"
CHOLESTYRAM	50.7 +/- 4.1'	39.0 +/- 3.1[a]	54.4 +/- 2.7[b]	6.6 +/- 1.4b
CHITOSAN	68.7 +/- 2.4[b]	18.3 +/- 3.0'	79.2 +/- 3.3'	2.5 +/- 0.7'
UMITORANOO	44.5 +/- 5.3'	45.1 +/- 2.0"	49.9 +/- 2.4[bd]	5.0 +/- 0.8

*[b~c~]d Values represent the mean +/- SEM of 6 rats per group. Values within same column not sharing a common superscript letter are significant at p < 0.01 - 0.05

● Sugano *et al* al.

CHOLEST = CHOLESTEROL TRIGL=TRIGLYCERIDES

UMITORANOO = UMITORANOO ALGAE COPRO = COPROSTANOL

PHYTO=PHYTOSTEROLS

Table II

EFFECT OF FIBER ADDITIVES ON CHOLESTEROL AND TRIGLYCERIDE LEVELS*

ADDITIVE (4%)	CHOLESTEROL LEVELS SERUM MG/DL	CHOLESTEROL LEVELS LIVER MG/G	TRIGLYCERIDE LEVELS SERUM MG/DL	TRIGLYCERIDE LEVELS LIVER MG/G
CELLULOSE	244 ± 35	44 ± 11	563 ± 72	172 ± 33
PECTIN	175 ± 13”	42 ± 7	404 ± 78’	156 ± 17
Al -PECTIN[f]	164 ± 10’	36 ±6[c]	382 ± 58’	138 ± 12[b]
CHITOSAN	137 ± 9[e,d]	15 ± 4[a,d]	303 ± 33”	87 ±20[a,d]

[a]p<0.01 vs Cellulose
[b]p<0.01 vs Cellulose
[c]p<0.01 vs Cellulose
[d]p<0.01 vs Al -Pectin
[e] p<0.02 vs Al -Pectin
[f]Al content of this diet was 0.2%

*Nagyvary et al. (17)