CHAPTER 4

PECTIN

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I. CHEMISTRY AND NOMENCLATURE

Pectic substances originate primarily in the cell walls and fibrous portions of fruit, vegetable, and other land plant tissues. They are complex colloidal carbohydrate derivatives containing as their major structural feature acid polysaccharides composed primarily of galaturonic acid units. Neutral sugars such as arabinose, galactose, rhamnose, and xylose have been identified as associated with the pectin molecule (1). Aspinall's work indicates that the rhamnose may be a part of the main chain structure of the pectin molecule. The association of arabinose and galactose may be either a sidechain attachment or an incidental part of the main chain. By this it is meant that the entire sugar molecule is not involved in the chain structure.

Part of the plant pectins are readily extracted with water. This readily soluble pectin in fruits increases as the fruit matures. The water-insoluble portion is known as protopectin, which consists of pectin bound with other tissue constituents, such as cellulose, to give rigidity to the tissue structure. Pectin will be released from protopectin by prolonged hydrolysis with hot water, by treatment with mild acid or alkali, by enzymes, and by holding at about 90°C in 0.5% ammonium oxalate.

The chemical extraction of pectin by these reagents has been illustrated by Joseph (8). (See Figure 1.)

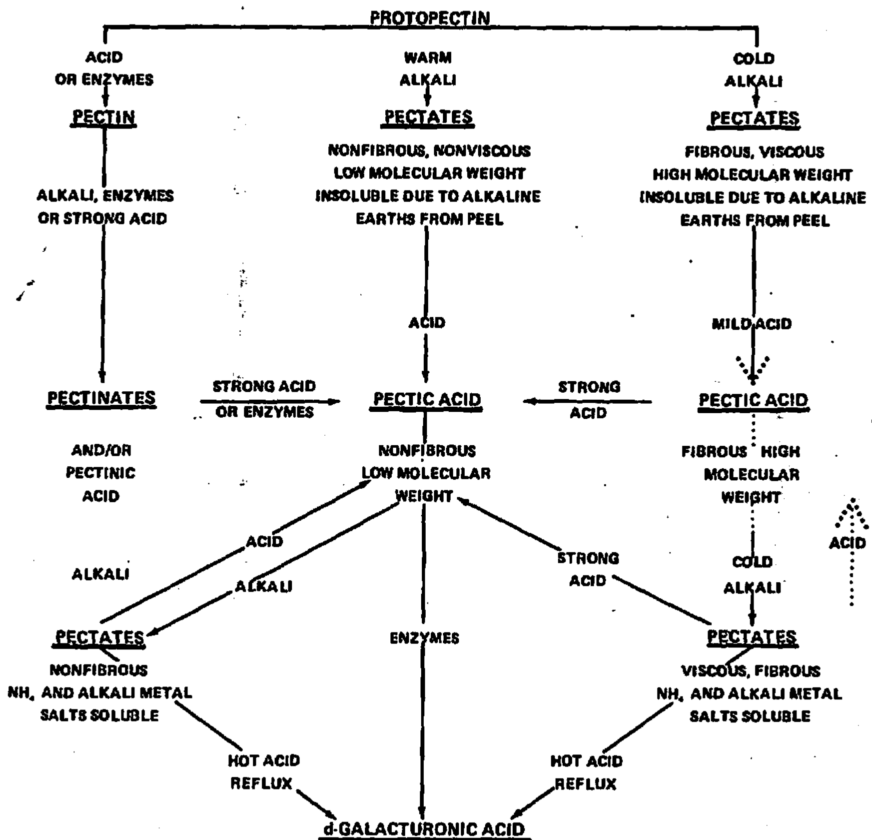

Figure 1. Interrelationship of the pectic substances. Reproduced with permission from Joseph (8).

When the carboxyl groups of the polygalacturonic acid chain are more than negligibly esterified by methyl groups, the term pectinic acid is applied. The salts formed from partially esterified pectins are referred to as pectinates. Salts of the completely de-esterified pectin molecule are pectates.

A guide to pectin nomenclature was developed by Joseph (8). Figure 2 comprises a nomenclature chart for pectic substances and the degrees (percentages) of esterification.

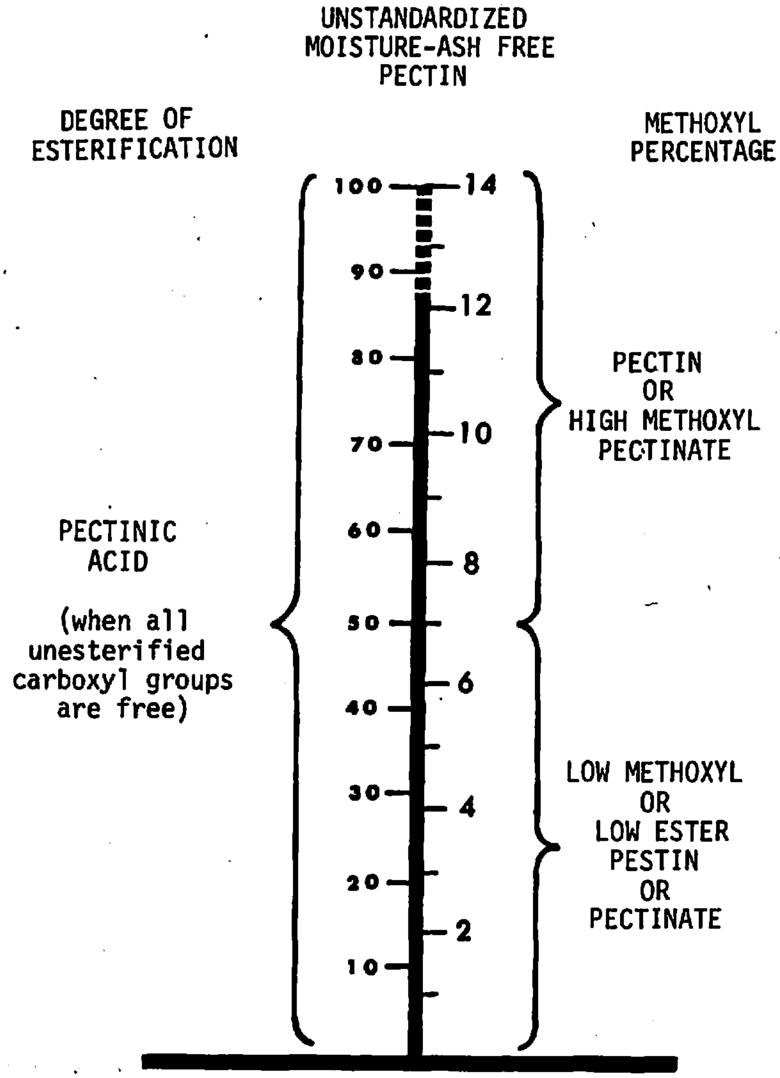

Figure 2. Nomenclature chart for the pectic substances.

II. PECTIC ENZYMES

Pectic enzymes occur in a number of plants and microorganisms and may be classified into pectin methylesterases and polygalacturonases. The pectin methylesterases hydrolyze the methylester linkages, whereas the polygalacturonases cleave the glycosidic bonds between the galacturonic acid molecules. Pectin transeliminases bring about the cleavage of the alpha (1→4) linkages, forming unsaturated derivatives of polygalacturonic acid. Recent work has shown that some of the pectic enzymes considered to be polygalacturonases may be reclassified as transliminases, since both these enzymes reduce the viscosity of pectin and produce a molecule of sugar for each alpha (1→4) linkage cleaved. Pectic enzymes can be subdivided further depending upon whether they act on the methylated or free polygalacturonic acid substances or whether they act on internal linkages. The pectic enzymes of commerce come from Aspergillus niger and are generally employed as a mixture of enzymes. Pectic enzymes may be added to a product to provide clarity or may be destroyed to preserve viscosity (17).

III. PECTIN CONTENT OF PLANT MATERIALS

Although pectins are found in the cell walls of all higher land plants, there is great variation in the pectic content of different plant varieties as well as in various plant materials. (See Table 1.) Of the various plant materials, one third of the dry weight of the albedo or white portion of citrus peel and 17% of dried apple pomace is pectin. From these two sources the major portion of commercial pectin is produced today.

IV. GEL FORMATION

A well-known characteristic of pectin is its ability to form jelly in the presence of acid and sugar. As discussed previously, the carboxyl groups of the polygalacturonic acids may be partially esterified by methyl groups as in pectinic acid. It is the degree of esterification that provides the name for the high-ester or high-methoxyl (HM) and distinguishes them from the low-ester or low-methoxyl (LM) pectins of commerce.

TABLE 1. PECTIN CONTENT OF FRUITS AND VEGETABLES
(percent of fresh weight as calcium pectate)

Plant variety	%
Apples	0.71 - 0.84
Apricots	0.71 - 1.32
Asparagus	Trace
Bananas	0.59 - 1.28
Beans	0.27 - 1.11
Blackberries	0.68 - 1.19
Carrots	1.17 - 2.92
Cherries	0.24 - 0.54
Cucumbers	0.10 - 0.50
Dewberries	0.51 - 1.00
Grapes	0.09 - 0.28
Grapefruit	3.30 - 4.50
Lemons	2.80 - 2.99
Loganberries	0.59
Oranges	2.34 - 2.38
Raisins	0.82 - 1.04
Raspberries	0.97
Squash	1.00 - 2.00
Sweet potatoes	0.78

Although both types of commercial pectins will form the pectin-sugar-acid jellies, gelation occurs under different conditions. The high-methoxyl or typical commercial pectin, in order to form gels, must meet two requirements. First, the sugar content or soluble solids level must be over 50% of the weight of material in the preparation, and second, the acid level must be adjusted to pH 2.9 to 3.4 depending on whether the pectin is rapid or slow setting.

Low-ester or low-methoxyl pectins, on the other hand, form gels when an alkaline earth cation, usually calcium, is included in the gel media. Sugar is not required in manufacturing gelled products using the low-ester pectin, and this pectin forms suitable gels over a pH range of 2.5 to 6.5. Despite the fact that pectin was discovered before the turn of the eighteenth century and has been used both in the home and commercially for jelly manufacture for countless years, the exact mechanism of gel formation is still not fully understood.

V. PECTIN METABOLISM

Experimental work on rats, dogs and man reveals that pectin does not appear to be absorbed by these species. A feeding trial carried out on weanling rats (18) using 0%, 5%, and 10% citrus pectin-S (55% esterified) and 10% citrus pectin-M (65% esterified) showed that 100% of the undigested compound could be recovered in the feces of these animals. Galacturonic acid, a metabolite of pectin, was not absorbed in any appreciable quantities from the human or canine ileum or the canine colon (19). Pectin administered to dogs passed through the stomach and part of the small intestine and was recovered without loss (9).

Kertesz reported that saliva and gastric juice do not act enzymatically on pectin (9). Nor did in-vitro studies with trypsin and pepsin reveal any hydrolytic effect of these intestinal enzymes on pectin. However, pectin incubated with fecal material is rapidly digested. Bacteria capable of metabolizing pectin in vitro were isolated from dog feces when the animal was fed pectin as its sole dietary item for one week (20). The more active bacteria belonged to aerobacillus, lactobacillus, micrococcus, and enterococcus. Berkefeld filtrates of these organisms were shown to contain heat-labile, pectinase-like enzymes, liquefying enzymes and/or pectase-like, coagulating enzyme. Some galacturonic acid and formic and acetic acids were the chief products.

The definitive studies in man (19), using the ileostomy technique, demonstrated that pectin is decomposed chiefly in the colon and that bacterial rather than animal enzymes are involved. Detailed studies carried out in the rat (6) showed that apple pectin is attacked by the intestinal flora and metabolized into galacturonic acid, other organic acids that are capable of resorption, and finally carbon dioxide and water.

Much controversy surrounds the values proposed for the digestible energy of pectin. In a study with rats fed citrus pectin-S and pectin-M at dietary levels of 5 and 10%, Viola (18) calculated the apparent digestible energy of pectin. In these experiments the contribution of pectin-M and pectin-S were both negative and were reported as -1.60 and -1.65 kcal/g, respectively.

Viola's work substantiated earlier work carried out by the Western Regional Research Laboratories in California (3). These workers fed 10% of citrus pectin to rats and concluded that this material was apparently not utilized by the rat. They based their conclusions on the fact that practically all the pectin fed could be accounted for in the feces.

In opposition to these two studies is the one carried out by Gaedeken (6) on the rat using apple pectin at dietary levels of 12.0 and 23.7%. Calculations from these studies showed a digestible energy which was calculated to 3.55 and 3.48 kcal for the 12.0-and 23.7-% dietary levels, respectively. Calculations from studies carried out in Sunkist Laboratories (15) using low-meth-oxy pectin and Pectin N.F. administered to human volunteers at a dosage level of 5 g 3x/day with meals showed the digestible energy of these compounds to be 2.86 kcal/g and 3.03 kcal/g, respectively.

Besides the numerous uses of pectin in food products, much work has been carried out to study the hypocholesterolemic activity of this material both in man and laboratory animals. In a 4-week study, Fisher <u>et al</u>.(5) noted a hypocholesterolemic activity in pigs. Four groups of each sex of Yorkshire pigs 8 weeks of age or four Hampshire pigs 16 weeks old were fed 5% pectin or 5% cellulose in a diet with and without cholesterol. Swine on the pectin-plus-cholesterol diet showed a lowering of their serum cholesterol levels when compared to those animals on a cholesterol-free diet. These trials suggest that an exogenous dietary source of cholesterol is necessary for the lowering of serum cholesterol in this experimental animal.

A 28-day study was carried out by Leveille and Sauberlich (12) in male rats fed 1% cholesterol with or without pectin. Those animals fed pectin showed a lowering of plasma and liver cholesterol. <u>In-vitro</u> studies revealed that pectin decreased by approximately 50% the transport of taurocholic acid. Similar results were noted <u>in vivo</u> when pectin and cholestyramine, an inhibitor of bile acid transport, were fed to rats. Radioactive studies utilizing cholesterol-4-C^{14} in male Wistar rats showed that oral pectin reduced the absorption of the labeled cholesterol by 7% from control values (7).

Middle-aged men fed 15 g of citrus Pectin N.F. per day for several weeks had a decrease in their cholesterol levels of 5% below their control value (a 15-g cellulose diet) (11). Diets were similar in fats, cholesterol, and calories but differed in the carbohydrate source. A considerable amount of carbohydrate in one diet was provided by legumes. The other diet had this carbohydrate source matched by sugar. In both diets, citrus Pectin N.F. reduced the cholesterol level in the subjects under trial.

Palmer and Dixon (16) administered citrus Pectin N.F. orally to human volunteers. The pectin was administered in a randomized, double-blind program in capsules at 2-g increments including the same number of placebo capsules containing Alphacel®. The six 4-week test periods were followed by a 10-week period without treatment. Serum cholesterol levels were significantly reduced in 12 out of 16 of the test subjects when the daily intake was 6 or more g of pectin.

Other pharmacological studies have been carried out in laboratory animals to determine if pectin possesses other activities besides its effect on serum cholesterol. Citrus Pectin N.F. fed orally to rabbits reduced gallstone formation when compared with the controls (4). Other investigations have been carried out to study the antiulcer effect of plantaglucide, the powdered pectin from the leaves of the large plantain (14). Stomach ulcers were induced in rats by injecting phenylbutazone intramuscularly. The authors concluded that plantaglucide had a distinct antiulcer effect on this experimental animal.

[redacted] Much of the work in this area has been carried out by Bender (2), who hypothesizes that pectin moves rapidly to the large intestine, coating the mucosa with unchanged polysaccharide. There, it is used as a carbon source by the normal flora. In addition to D-galacturonic acid, lower organic acids, especially acetic and formic acids, are formed producing the normal complement of acids that stabilize the pH of the colon. These acids are also bacteriostatic against most pathogens at normal bowel pH. Since disorders associated with abnormal and undesirable flora are usually accompanied by a higher-than-normal pH, the inflow of pectin and the subsequent return to normal pH by its digestion adversely affect the growth of the pathogens and encourages the normal flora to return to full activity.

There are two apparent causes for this return to normalcy: the lowering of pH and the production of certain acid radicals at levels that cannot be tolerated by most of the pathogens. However, some effects remain that are not explained by this mechanism, such as the extremely prompt but usually only temporary relief that results from a single dose, with the need of two or more doses for complete relief; the almost immediate reversal of the fatigued feeling to one of well-being, and the inhibiting effect of pectin on certain viruses. The mechanism of the action of pectin as an antidiarrheal in man still requires much investigation.

VI. CONCLUSION

In 1951 Kertesz compiled most of the information that was available on pectin to that date (10). The work reported in this chapter shows that pectic substances have been and remain a fascinating group of natural compounds. Of particular interest are the role that these materials play in the daily dietary and the contribution they make to the nutritional component of fiber. Much work remains to determine the role of pectin in the plant cell walls. An excellent recent review by Nelson et al. (13) on commercially important pectin substances shows that much research needs to be done into the chemical structure of pectin. Certainly a great deal of work is necessary to determine the absorption, metabolism, and excretion of pectin substances and their metabolites in man, and further metabolic studies to determine the digestible energy of these natural colloids in the human subject.

Pharmacological activity such as the chelation of certain heavy metals by pectin, hypocholesterolemia and the antidiarrheal effect of pectin are fruitful fields for further studies in order to determine the role of pectin in the pharmaceutical armamentarium.

TOPICS IN DIETARY FIBER RESEARCH

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PLENUM PRESS · NEW YORK AND LONDON