

a weak brine and usually consumed immediately, although they can be frozen or processed in cans for later consumption.

Peanuts are an excellent source of high-quality native protein that has potential application as an additive in food products. As mentioned earlier, the peanut plant itself has a high nutritional value and can be used for feed for livestock or plowed back into the soil to aid in fertilization of future crops as a result of nitrogen formation.

The peanut shells accumulate in tremendous quantities at shelling plants and many applications for by-product use have been considered. The relatively light weight per volume of the shells makes transportation an economic consideration and limited seasonal availability is a factor. The chief use of peanut shells is for fuel for boilers with limited uses for roughage in cattle feed, poultry, and kitty litter, and filler in artificial fire logs (8). Additional potential uses include charcoal, medium for growing mushrooms, mulch, carrier for pesticides and fertilizers, absorbent for molasses feed, anticaking materials, floor-sweeping compounds, foundry-sand component, sealant for oil drilling muds, metal polish, activated charcoal, and chemical replacement of phenolic resins (8).

AFLATOXIN

Under certain environmental conditions in the field or under improper storage conditions, two species of fungi, *Aspergillus flavus* and *A. parasiticus*, can colonize peanuts and produce the carcinogenic mycotoxins, collectively called aflatoxins (10). Prior to the late 1970s it was thought that the aflatoxin problem in peanuts was primarily associated with poor window-drying conditions and, to a lesser extent, to improper storage due to condensation or roof leaks. Subsequent research on the association of the aflatoxin problem with particular climatic conditions prior to harvest, in addition to some recent research, have resulted in a reevaluation of the etiology of aflatoxin contamination in peanuts (11). Preharvest contamination is now considered the most significant source of contamination, particularly in the Southeast and Southwest. Storage contamination is usually a less-significant problem. The aflatoxin problem has been most prevalent during growing seasons associated with late-season drought stress, such as 1972, 1977, and 1986 in the southeastern peanut belt and in all three peanut producing areas (Texas-Oklahoma, Georgia-Alabama-Florida, and North Carolina-Virginia) during 1980.

There are two types of preharvest aflatoxin contamination in peanuts, that associated with insect damage and that which occurs in the absence of obvious damage. Contamination associated with insect damage is more easily removed during the milling process by electronic color-sorting techniques, while contamination of visibly undamaged seed is more difficult to detect and remove during the milling process.

CURRENT AND FUTURE TRENDS

Increased consumer awareness and demands for improved quality of all food products have resulted in the recent formation of a National Peanut Council, Inc. sponsored

Peanut Quality Task Force to identify the most pressing parameters affecting peanut quality. This task force recommended that the peanut industry should support research and implement changes that strive for a future goal of zero defects in aflatoxin, foreign material, chemical residues, flavor and physiological seed maturity. Also, the existing systems for controlling quality should be adjusted as deemed necessary to help achieve these goals.

BIBLIOGRAPHY

1. R. O. Hammons, "Origin and Early History of the Peanut," in H. E. Pattee and C. T. Young, eds., *Peanut Science and Technology*, American Peanut Research Education Society, Yoakum, Tex. 1982, pp. 1-18.
2. J. P. Beasley, Jr., "Georgia Peanut Varieties," Bulletin 965, Cooperative Extension Service, University of Georgia, 1987, pp. 1-20.
3. "USA Peanuts," *National Peanut Council Technical Bulletin*, 1988, pp. 1-21.
4. T. H. Sanders, A. M. Schubert, and H. E. Pattee, "Maturity methodology and postharvest physiology," in Ref. 1, pp. 624-654.
5. E. J. Williams and J. S. Drexler, "A Non-destructive Method for Determining Peanut Pod Maturity," *Peanut Science* 8, 134-141 (1981).
6. W. A. Parker, "Peanut Blanching—Processing, Utilization and Effects of Quality and Product Shelf Life," in E. M. Ahmed and H. E. Pattee, eds., *Peanut Quality: Its Assurance and Maintenance from the Farm to End-Product*, Bulletin 874, Agric. Exp. Sta. Inst. Food Agric. Sci., University of Florida, Gainesville, 1987, pp. 51-54.
7. W. Parker, Seafood Blanching Corp., Edenton, N.C.
8. J. G. Woodroof, *Peanuts: Production, Processing, Products*, AVI Publishing Co., Inc., Westport, Conn., 1983.
9. R. Latham, unpublished data, Statistical Reporting Service, Washington, D.C.
10. U. L. Diener, R. J. Cole, T. H. Sanders, G. A. Payne, L. S. Lee and M. S. Klich, "Epidemiology of Aflatoxin Formation by *Aspergillus flavus*," in R. J. Cook, G. A. Zentmyer and E. B. Cowling, eds., *Annual Review of Phytopathology* 25, 249-270 (1988).
11. J. W. Dorner, R. J. Cole, T. H. Sanders and P. D. Blankenship, "Interrelationship of Kernel Water Activity, Soil Temperature, Maturity, and Phytoalexin Production in Preharvest Aflatoxin Contamination of Drought-Stressed Peanuts," *Mycopathologia* 105, 117-128 (1989).

RICHARD J. COLE
JOE W. DORNER
USDA, ARS, National Peanut
Research Laboratory
Dawson, Georgia

PECTIC SUBSTANCES

Pectic substances are a group of complex polysaccharides localized to the middle lamella, intercellular crevices, and primary cell walls of most if not all higher plants (1). They are significant contributors to the texture of fruits, vegetables, and their processed products (2). In the diet, pectic substances serve as food fibers with evidence that they provide additional benefits by lowering blood cholesterol

PECTIC SUBSTANCES

and reducing glucose intolerance in diabetics (3). In addition to the obvious structural role of pectic polysaccharides in plants, pectic fragments act as chemical messengers in the development, growth, senescence, and biochemical protection of plants. (4).

GLOSSARY OF TERMS

Because the gel-forming properties of pectic substances (*pectin* is derived from a Greek word meaning "to congeal or solidify") were discovered prior to the development of modern organic and macromolecular chemistry, common rather than structural names were applied to pectic polysaccharides and these persist. (5).

Pectic Acid. Pectic acid is pure poly[(1-4)-*o*-linked (α -*D*-galactopyranosyl uronic acid)] and is often referred to as polygalacturonic acid.

Pectate. Pectate as in calcium or sodium pectate is pectic acid that is fully or partially neutralized with metal ions. Often referred to as polygalacturonate as in calcium or sodium polygalacturonate.

Pectinic Acid. Pectinic acid is a mixture of pectic substances, a significant portion of which is a copolymer of galacturonic acid and its methyl ester.

Pectin. Pectin, as originally defined, is a water-soluble mixture of pectinic acids or partially neutralized pectinic acids capable of undergoing gel formation.

Pectinate. Pectinate as in calcium or sodium pectinate is pectinic acid that is partially or fully neutralized with metal ions.

Protopectin. Protopectin pectin refers to native, undissolved or insoluble plant tissue pectin.

DISTRIBUTION IN NATURE

The percentage of pectic substances in plants vary with species, variety, anatomy, and maturity. The highest concentration of pectic substances are found in young tissue and in fruit tissue. Typically, whole mature fruit contains 3–7% pectic substances on a dry-weight basis and 0.13–1.1% on a fresh-weight basis. The relatively high pectic and low caloric content of citrus fruits make them a good source of soluble dietary fiber in that pectic substances are not digested until they reach the lower gastrointestinal tract. Apple pomace (the residue of pressed apples) may contain up to 20% pectic substances and the albedo of oranges (the white, spongy material on the inside of the peel) may contain up to 40% pectic substances on a dry-weight basis.

ISOLATION AND PURIFICATION

The relative ease of the isolation and purification of large quantities of food-grade pectic substances account for their early discovery. Commercially, apple pomace or cit-

rus peels (eg, orange, grapefruit, or lime) are extracted with the goal of producing food-grade pectin for gels (6). Typically, pectin is acid extracted at low pH (1.5–3) to inhibit degradation by endogenous enzymes, ester saponification, and alkaline degradation by beta-elimination reactions. Extracts are filtered or centrifuged to remove insolubles, precipitated with alcohol or polyvalent salts such as those from aluminum or copper.

To obtain pectins with maximum retention of native structure and properties for research purposes, milder techniques have been adopted at the expense of product yield and with considerable lengthening of the isolation-purification process. In these procedures, relatively intact cell walls are isolated by macerating plant tissues in aqueous alcohol, washing to remove extraneous debris and deactivate endogenous enzymes, then sequentially extracting with chelating agent and mild alkali. Attempts to reduce size heterogeneity by gel filtration chromatography and chemical heterogeneity by ion exchange chromatography have been met with limited success.

CHEMICAL COMPOSITION AND STRUCTURE

Mildly extracted pectic substance is primarily a helical block copolymer of *D*-galacturonic acid and its methyl ester (7). These comonomers are (1 → 4)*o*-linked as poly(α -*D*-galactopyranosyluronic acid) and its methyl ester. Blocks are interrupted by (1 → 2) *o*-linked α -*L*-rhamnopyranosyl inserts. Some of these features are incorporated in Figure 1. Neutral sugars associated with pectin other than rhamnose include galactose, arabinose, glucose, xylose, and mannose. At least three of these neutral sugars, arabinose, galactose, and xylose, have been found in pectin as short side chains that themselves may be branched. Side chains in apple pectin are not equally distributed (8). Some portions of the pectin backbone have a high density of side chains and have been designated as hairy regions whereas other portions of the pectin backbone are completely devoid of side chains and have been labeled as smooth regions. A few sources of pectin (eg, sugar beets) contain acetyl and feruloyl esters. Acetyl esters are probably linked to ring hydroxyls in the galacturonate backbone whereas feruloyl esters appear to be linked to neutral sugar side chains. Approximately 80–90% (by weight) of total sugars in commercial citrus pectins are residues of galacturonic acid and its methyl ester with the remaining sugars being neutral. Degree of methyl esterification (DM) in pectic substances will vary with plant source and method of extraction. Commercial citrus and apple pectins with DM ranging from 80 to 18% are available. X-ray diffraction patterns of sodium polygalacturonate indicate that water molecules are bound to each galacturonate residue in the backbone (9). Thus bound water may account for about 8% of pectin samples by weight.

METHODS OF ANALYSES

Because of its complex composition, several methods are necessary to analyze for pectin (10). A few of the more important methods will be discussed here. Of the several colorimetric methods developed to analyze for galacturonic acid, the reaction of pectin with *m*-hydroxyl-

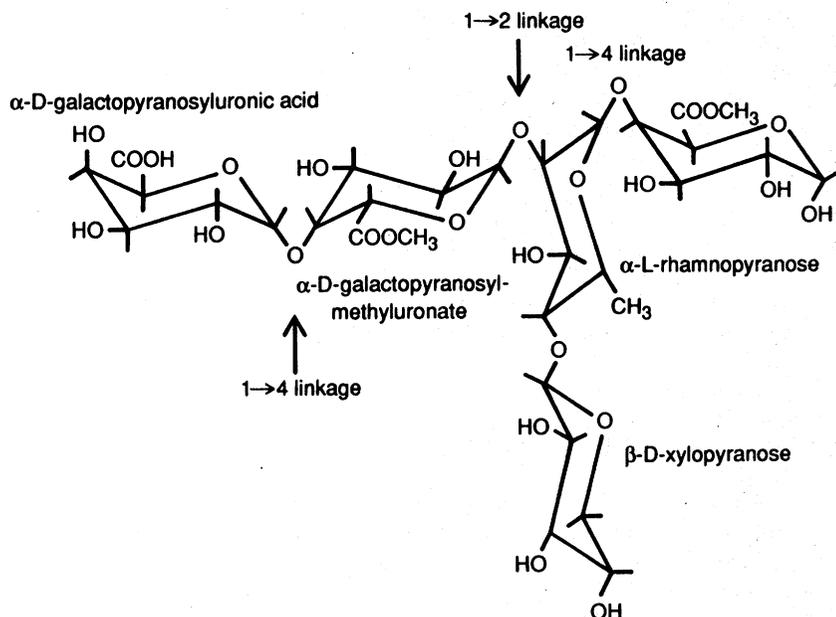


Figure 1. Portion of pectin molecule.

biphenyl in heated acid media to form a colored product is employed widely. Base titration before and after saponification is used for the simultaneous determination of DM and galacturonic content. Also, DM is determined by saponifying methyl ester groups and analyzing for free methanol by gas chromatography or by oxidizing the methanol to formaldehyde, which is determined colorimetrically. Carboxyl and methylester groups also may be determined by infrared red spectroscopy in deuterated water provided there is a prior-calibration against known standards. Often, neutral sugars are analyzed by gas chromatography after hydrolysis and conversion to volatile derivatives. Various derivatives and stationary phases have been employed. In one method, sugars are converted to their alditol acetates and chromatographed on a high-performance capillary column. Acetyl esters are analyzed by conversion to acetic acid, separation by steam distillation and titration of the acid. Feruloyl esters are hydrolyzed to ferulic acid, which is analyzed by the Folin-Ciocalteu reagent.

CHEMICAL AND ENZYMATIC REACTIONS

The reactions of pectin are those characteristic of polysaccharides, esters, and organic acids (7). A select few of the more important reactions will be discussed, briefly. Pectin undergoes acid-, base-, and enzyme-catalyzed depolymerizations. At acidic pH, glycosidic bonds other than those of (1 → 4) self-linked alpha-*D*-galacturonic acid are hydrolyzed preferentially. Thus commercial pectin is extracted from plant matrices by controlled acid hydrolysis. Prolonged acid hydrolysis can produce polygalacturonic acid with about 25 residues. Base-catalyzed depolymerizations occur at neutral and higher pH. These are beta-elimination reactions, which proceed with concurrent endodepolymerization, deesterification, and double bond formation (Fig. 2). The relatively high susceptibility to enzymatic and acid-catalyzed hydrolysis of the neutral sugar side chains and rhamnoglacturonan glycosidic bonds in the backbone of pectin may play an important role in plant metabolic processes. Evidence is accumulating that vari-

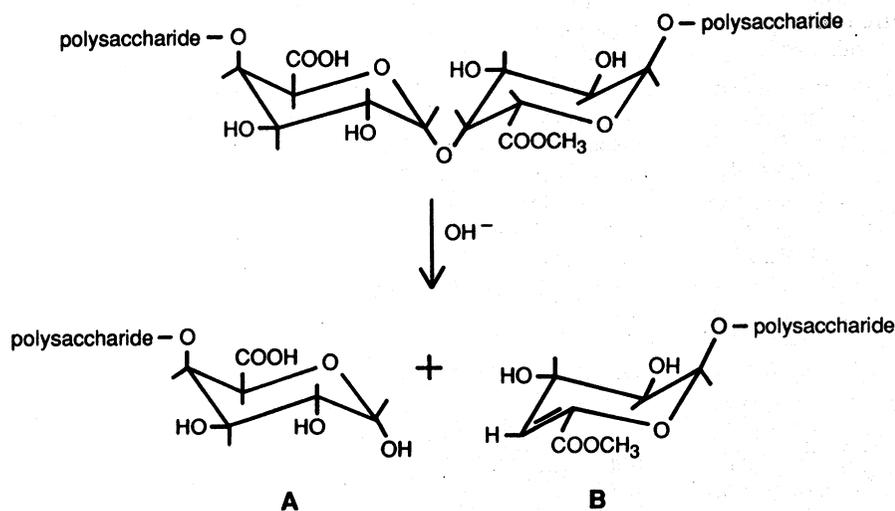


Figure 2. Schematic of beta-elimination reaction: (a) is reducing sugar end group; (b) is unsaturated, nonreducing sugar end group.

PECTIC SUBSTANCES

ous pectic fragments act as biochemical messengers that initiate various biochemical reactions in plant development, senescence, and in the defense of plants against pathogens (4). For example, evidence suggests that fragments from pectin-containing galactose may elicit ethylene production, which is important in the process of senescence. Endogenous endopolygalacturonases have been associated with fruits that ripen rapidly (eg, pears and freestone peaches) whereas those that contain only exopolygalacturonases (eg, apples and clingstone peaches) ripen more slowly. Polygalacturonases depolymerize deesterified pectins, only. Most of the common pectin lyases depolymerize pectin in a fashion similar to beta-elimination reactions (Fig. 2). Commonly, pectin lyases are not found endogenously in plant cell walls but are produced by microorganisms. In addition to their biological importance, bacterial pectolytic enzymes have gained importance as probes to elucidate the neutral sugar side chain structure of pectin (8). For example, the action of beta(1,4)-galactanase has shown that apple pectin contains arabinogalactan side chains high in arabinose. Pectin methyl esterase activity has been found in the plant cell wall, but the biological function of this enzyme is not clear. Reactions specific to the reducing sugar end group are important in that they permit determination of the number-average molecular weight and provide a method of following the course of depolymerization reactions. Chlorite oxidation of end groups has been used to determine pectin molecular weight, whereas several color reactions specific for reducing sugars have been used to assay for the galacturonic acid produced in depolymerization reactions (6). Ammonia partially amidates through displacement of pectin methyl ester groups. Amidated low methoxy pectic substances gel more readily than corresponding nonamidated low methoxy pectic substances (7). Recently, pectin from sugar beet pulp has been gelled by intermolecular, oxidative coupling of feruloyl ester groups through their aromatic rings. Coupling was achieved with a mixture of hydrogen peroxide and peroxidase (6). This reaction provides an opportunity for commercialization of beet pectin, because it is a poor gel former without oxidative coupling.

MOLECULAR WEIGHT, SIZE, AND SHAPE OF PECTINS

Over a period spanning more than 50 years of research, the molecular parameters of pectins have been measured extensively by numerous methods. Nevertheless, significant disagreements prevail concerning these parameters. The controversy may arise from the variability of pectin with plant source, whether dissolved pectin exists in solution as individual molecules or as aggregates, and the tendency of pectin to fragment. High methoxy (ca DM = 73) commercial citrus pectins give number-average molecular weights in the range $4\text{--}4.9 \times 10^4$ (11). A linear plot of reduced osmotic pressure against concentration appears to indicate a well-behaved unaggregated polymer. The second virial coefficient calculated from osmometry indicated a rod-like shape. Nevertheless, briefly heating pectin resulted in a slow concentration-dependent disaggregation that was also shown by osmometry. High-performance size-exclusion chromatography (hpsec) with

on-line viscometry detection on a series of commercial citrus pectins gave results consistent with the aggregated rod model (12). Hpsec studies of tomato cell wall pectins with computer-aided curve fitting of the chromatograms, revealed that all pectins investigated were composed of a linear combination of five macromolecular subunits (13). The relative sizes of these subunits as obtained from their radii of gyration (R_g) were 1:2:4:8:16, with the smallest subunit having an R_g of about 25 Å. Dissociation of pectin into smaller size fragments by dialysis against 0.05 M NaCl led to the conclusion that cell-wall pectin acted as if it were an aggregated mosaic, held together at least partially through noncovalent interactions.

BINDING PROPERTIES

Many of its unique properties result from the propensity of pectin to self-aggregate or to interact with cosolutes (6). A case in point is the pectin gels, which are three-dimensional networks capable of entrapping water. High-methoxyl pectins (HMP), degree of methyl esterification in the range 80–57%, are induced to gel by adding sugars, which are thought to promote the self-aggregation of pectin by removing bound water, reducing ionic repulsions, and stiffening the polymer chain. These nonspecific interactions with sugars may be responsible for pectin's ability to reduce glucose intolerance in diabetics. For HMP at constant pH, gel strength and rate of gelling increase with DM, presumably through increased interchain hydrophobic interactions. HMPs of decreasing DM can be induced to gel by decreasing the pH, possibly through increased interchain hydrogen bonding. Low-methoxyl pectins (LMP), DM below 50%, gel with the addition of calcium or other divalent cations through interchain cross-links. Because decreasing DM increases the number of potential cross-links, LMP exhibits increased gel strength and higher gelling temperatures with decreasing DM. For HMP and LMP, gel strength increases with increased molecular size, possibly by cooperative self-interactions. It appears that all three major mechanisms exist for interchain interactions, namely divalent cation cross-links, hydrogen bonding, and hydrophobic interactions. Furthermore, for any mechanism to prevail, a critical number of functional groups must be present to promote cooperative interactions. Electron spin resonance studies support the concept that divalent cation binding to pectin in apple cell walls results in interchain bridges between adjacent smooth regions of pectin and that binding is a sequential cooperative process. Clinical studies suggest that pectin lowers blood cholesterol. This may be a case where the formation of divalent cation bridges is important in that calcium may form bridges between negatively charged pectin and bile acids. It has been suggested that binding and excretion of bile acids leads to a decrease of cholesterol in the bloodstream.

FOOD APPLICATIONS

A major application of pectin is in jams and jellies (14). A high-sugar jam contains 30–45% of fruit pulp and 0.20–0.4% pectin added as a gelling agent. Jams made with

HMP must contain at least 60% soluble solids (sugars) to gel. Reduced sugar or dietetic jams are manufactured with 55% or less soluble solids (even below 30%), by adding low methoxyl pectins (eg, in the range 0.75–1.0%). At very low soluble solids, a calcium salt is added often to aid gellation. Frequently, jellies are made from depectinized fruit concentrates with added pectin, water and sugar. High-quality, tender confectionery jellies with excellent flavor-release characteristics contain pectin. Pectin is added to jams, fillings, and toppings as a gelling or thickening agent in the preparation of bakery goods. HMP jams are useful in applications requiring resistance to the heat of baking such as occurs in producing tarts containing jam. Amidated low methoxyl pectins (ALMP) confer thermal reversibility to gels. These gels are useful as glazes for pastries or flans. Typically, these products are supplied as a paste containing ALMP, calcium diphosphate, and 65% sugar solids, which when diluted and melted can be reset to a clear shiny glaze on cooling. In recent years, pectin has found increased application as an additive to dairy products. Yogurt containing fruit bases has been growing in popularity. Substituting pectin for modified starch as a thickening agent in yogurts will maintain a uniform distribution of fruit throughout the yogurt without masking delicate fruit flavors. Furthermore, unlike starches, pectin will not introduce a floury texture to yogurts. If the fruit bases contain 60% sugar, then HMP can be added. If the sugar content is lower than 60%, then ALMP is added. HMP stabilizes casein against aggregation when heated at a pH less than 4.3. Thus it is added as a stabilizer in ultrahigh-temperature-treated yogurt drinks and to milks blended with fruit juices. Pectin also stabilizes acidified soy milk drinks and whey products against protein precipitation. A low level of pectin is often added to low-calorie soft drinks to replace lost mouth feel with the removal of sugar. Pectin is added to sorbet and ice pops to control ice crystal size; and in ice pops to prevent flavor and color from being sucked from the ice structure. Pectin is added to chutney and sauces to improve texture and batch-to-batch uniformity. LMP and ALMP gels can replace gelatin as a base in dessert jellies for the purpose of providing good flavor release. Pectin gels have higher melting points than gelatin gels and thus hold up better in warm weather.

Pectin has several applications in the pharmaceutical industry. It has been added to mixtures containing kaolin or bismuth compounds for the prevention of diarrhea. Pectin is added to maintain the viscosity of medicinal syrups. Recently, pectin has been employed as a filler in self-adhesive colostomy flanges and to promote healing by its addition to wound dusting powders and ulcer dressings.

BIBLIOGRAPHY

1. M. C. Jarvis, "Structure and Properties of Pectin Gels in Plant Cell Walls," *Plant Cell Environment* **7**, 153–164 (1984).
2. G. B. Fincher and B. A. Stone, "Metabolism of Noncellulosic Polysaccharides," in W. Tanner and F. A. Loewus, eds., *Plant Carbohydrates II*, Vol. 13, Springer-Verlag, New York, 1981, pp. 103–105.
3. M. Chang, "Dietary Pectin: Effect on Metabolic Processes in Rats," in I. Furda, ed., *Unconventional Sources of Dietary*

Fiber, ACS Symposium Series **214**, American Chemical Society, 1983.

4. E. A. Nothnagel, M. McNeil, P. Albersheim, and A. Dell, "XXII A Galacturonic Acid Oligosaccharide from Plant Cell Walls Phytoalexins," *Plant Physiology* **71**, 916–1026 (1983).
5. Z. I. Kertesz, *The Pectic Substances*, Wiley-Interscience New York, 1951, pp. 3–9.
6. M. L. Fishman, "Chemical and Physical Properties of Pectin," *ISI Atlas of Science: Biochemistry*, Vol. 1, 1988, pp. 215–219.
7. J. N. BeMiller, "An Introduction to Pectins: Structure and Properties," in M. L. Fishman and J. J. Jen, eds., *Chemistry and Function of Pectins*, ACS Symposium Series **310**, American Chemical Society, 1986, pp. 2–12.
8. J. A. deVries, C. H. den Uijl, A. G. J. Voragen, F. M. Rombouts, and W. Pilnik, "Structural Features of the Neutral Sugar Side Chains of Apple Pectin Substances," *Carbohydr. Polym.* **3**, 193–205 (1983).
9. M. D. Walkinshaw and S. Arnott, "Conformations and Interactions of Pectins," *Molekulyarnaya Biologiya* **153**, 193–205 (1981).
10. L. W. Doner, "Analytical Methods for Determining Pectin Composition," in Ref. 7, pp. 13–21.
11. M. L. Fishman, L. Pepper, and P. E. Pfeffer, "Dilute Solution Properties of Pectin," in J. E. Glass, ed. *Water Soluble Polymers: Beauty with Performance*, Advances in Chemistry Series **213**, American Chemical Society, 1986, pp. 57–70.
12. M. L. Fishman, D. T. Gillespie, S. M. Sondey, and R. A. Barford, "Characterization of Pectins in Conjunction with Viscosity Detection," *Journal of Agricultural and Food Chemistry* **37**, 584–591 (1989).
13. M. L. Fishman, D. T. Gillespie, and S. M. Sondey, "Macromolecular Components of Tomato Fruit Pectin," *Archives of Biochemistry and Biophysics* **274**, 179–191 (1989).
14. C. D. May, "Industrial Pectin Sources, Production and Applications," *Carbohydr. Polym.* **12**, 79–99 (1990).

MARSHALL L. FISHMAN
USDA/ARS/ERRC
Philadelphia, Pennsylvania

PEPTIDES

Peptides have relevance to food science in various ways. Peptides contribute to the physical properties of food (physical aspect) and have taste (organoleptic aspect). Intestinal absorption of dipeptides or tripeptides is better than that of free amino acids (nutritional aspect). Biologically active peptides are found in food (physiological aspects). In this article the general aspects of peptides will be briefly summarized and various aspects of peptides as food constituents will be described.

GENERAL ASPECTS OF PEPTIDES

Definition

Peptide is a substance in which plural numbers of amino acids are bound together by peptide bonds, amide bonds between α -amino groups, and α -carboxyl groups of neighboring amino acids. Peptides containing less than 10 amino acid residues are called oligopeptides and those containing 10 amino acids or more are called polypeptides.