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Plant carbohydrates—An overview

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Abstract. There are several reviews on the chemistry, biochemistry and uses of carbohydrates in general. The scope of the present review is restricted essentially to research done on the plant carbohydrates in India and information available in research journals. Emphasis is placed on the various classes of plant carbohydrates, viz free sugars, water-soluble polysaccharides, starch, pectins, gums and mucilages, hemicelluloses and cellulose. Different aspects of work on these polymers have been covered in a broad sense, such as chemistry and structure, biochemistry, nutrition and processing-modification-application.

Keywords. Carbohydrates; gums and mucilages; polysaccharides; starch; hemicellulose; cellulose.

1. Introduction

Carbohydrates are one of the major constituents of plants. They are formed by the photosynthetic activity of plants and represent the largest proportion of organic compounds. Over the past 3 decades carbohydrate research has advanced greatly and substantial progress is being recorded year by year. The variety of structures and physical properties exhibited by these molecules is such that they impinge on all aspects of our every day existence and our understanding of the nature of life itself depends on unravelling their inherent complexity and interaction with other organic compounds.

In plants, carbohydrates perform a variety of physiological functions (Berdanier 1976), such as cellulose forming part of the structural component, starch as reserve material providing an energy source, gums and mucilages performing a defensive action to prevent tissue desiccation, etc (see Smith and Montogomery 1959). Carbohydrate polymers possessing more subtle functions in nature are often structurally more complex.

In animals, consumption of carbohydrates in large excess alters the concentration of serotonin, a powerful neurotransmitter, stimulates insulin secretion, and decreases plasma fatty acids content (Berdanier 1976). In addition, as dietary fiber, they are of significant nutritional importance (Jeanes and Hodge 1975).

It is reported that oligosaccharide fragments of branched β-glucans and fungal cell walls control gene expression in plant cells. In other words it is suggested that the fragments of the plant cell wall polymers could possibly be used to regulate within plants, such functions as the rate of cell growth, time of flowering, the activation of mechanisms for resistance to virulent plant pathogens. Some of the non-cellulosic β-glucans in cell walls, together with other polysaccharides contribute to several physiologically important wall characteristics such as water-holding capacity, porocity and plasticity (Stone 1984).

Plant carbohydrates are generally divided into 3 main groups viz mono-, oligo- and polysaccharides. Monosaccharides (and some times their derivatives too) are the simplest building blocks of any carbohydrate macromolecules. The bonding (more specifically, the glycosidic linkage) invariably takes place between the C-1 hydroxyl of one sugar residue with any one of the hydroxyls of the succeeding sugar residues and thus giving rise to 1,4-, 1,3-, 1,2- or 1,6-linkages. Occasionally one of the available hydroxyls may be further involved in a glycosidic linkage which leads to branching. Unlike in proteins where there is no branching, in carbohydrates there is a great scope for branching because of the availability of many free hydroxyls. Further the existence of α- and β-anomeric forms, D and L-configurations, and pyranosyl and furanosyl ring forms can lead to a multitude of structural types. Most of the variants are seen in nature.

There is a great structural diversity within the polysaccharides, which is reflected in the multitude of functions they perform. In contrast to bacterial polysaccharides (Mayer *et al* 1985), which have regular structures (repeating units), the arrangement of sugar units in plant polysaccharides is often found to be more random. The biological significance of such structural irregularities is not clear at present. This apparent irregularity might possibly be due to the plant tissue in which the cells are at different stages of growth and differentiation and therefore perhaps contain different polymers. It is however tempting to speculate that in order to match the needs of the tissue, plants synthesize a variety of polysaccharide structures.

Investigations carried out in this field have provided a wealth of information and have contributed to a certain extent to our understanding of their chemical structure-biological function relationships. Many polysaccharides have had commercial importance for centuries and subtle aspects of their properties were long known before the advent of molecular predictions. For example, the use of cellulose in fiber and paper manufacture, and that of pectins and alginates in the food industries as gelling and emulsifying agents were known long ago. For a clearer understanding of the role of carbohydrates *in situ* and/or *in vitro* conditions a careful indepth study of a multidisciplinary nature is essential.

2. Free sugars: Mono- and oligosaccharides

2.1 *Chemistry*

The free sugars, such as mono-, di- and oligosaccharides occur almost universally in different tissues of plant materials. The sugars are normally extractable with 70–80% aqueous alcohol. The common mono- and disaccharides such as glucose, fructose, galactose, sucrose, lactose and maltose are hydrolysed and absorbed, but the oligosaccharides of the raffinose series, viz raffinose, stachyose and verbascose, are unavailable for digestion and absorption, and therefore lead to flatulence, a social discomfort (Jeanes and Hodge 1975). The latter is due to lack of α-galactosidase in human gastrointestinal tract. Extraction with water or aqueous alcohol, or alternatively seed germination eliminates the flatus-inducing components. In plants the free sugars represent a buffer stock of ready source of energy, particularly in their initial stages of growth.

A series of non-reducing disaccharides have been isolated from the dried twigs of

Sarcostemma brevistigma (Khare *et al* 1980a,b). The pregnane glycosides extracted from the twigs were subjected to mild acid hydrolysis, yielding a mixture of oligosaccharides which were separated on a column of silica gel. Three sugars, viz brevobiose, tigmobiose and sarcobiose (Khare *et al* 1980a,b,c) were isolated in pure forms and their structures established on the basis of chemical and spectroscopic evidence.

Brevobiose: 4-0-(6-deoxy-2-0-methyl-β-D-allopyranosyl)-D-boivonose,
Tigmobiose: 2,6-dideoxy-β-D-ribohexapyranosyl-2,6-dideoxy-β-D-ribohexapyranoside,
Sarcobiose: 3,4-anhydro-2,6-dideoxy-β-D-lyxo-hexapyranosyl-6-deoxy-3-0-methyl-β-D-allopyranoside.

Similarly, from the shade-dried stems and twigs of *Gymnema tingens* (family—*Asclepiadaceae*) pregnane glycosides were extracted, acid-hydrolysed and chromatographed on silica gel to get a new disaccharide designated sugar T, identified as 3,4-anhydro-2,6-dideoxy-β-D-ribohexapyranosyl-6-deoxy-3-0-methyl-β-D-allopyranoside (Khare *et al* 1980d).

From the dried root bark of *Pavetta indica* Linn., D-mannitol was isolated (1%) (Banerjee and Ghosh 1956). A 56% methanolic extract of north Indian vetiver roots contained glycerol, fructose, glucose and sucrose (2·8 : 30·6 : 15·6 : 50·9) (Audichya *et al* 1971). The occurrence of glycerol is of considerable biological significance.

From the tender kernel of palmyra palm (*Borassus flabellifer*) (Subrahmanyan *et al* 1956) free sugars have been isolated and characterized to be sucrose (0·4%), fructose (1·5%) and glucose (3·2%). The sugar constituents of the glycoside from the seeds of *Luffa cylindrica* (Barua 1957) were galactose, arabinose, xylose and rhamnose. The nectar of coconut (*Cocos nucifera*) (Prasannakumari 1963) contained fructose, sucrose and glucose.

The saponin isolated from the seeds of *Acacia leucophloea* Willd. is characterized as oleanolic acid—oligosaccharide. The sugar moiety of the saponin was composed of glucose, galactose, xylose and rhamnose (Gopalchari and Dhar 1958).

A thin-layer chromatographic method has been developed for the separation of anomeric aryl tetra-O-acetyl-D-glucopyranose (Audichya 1971).

The nature of free oligosaccharides present in cashew nut (*Anacardium occidentale*) has been studied (Shivashankar *et al* 1978). Sucrose was present in major amounts followed in decreasing order, by raffinose, stachyose and verbascose. These free carbohydrates are thought to be responsible for the characteristic flavour development during processing (roasting) (Shivashankar *et al* 1978).

2.2 *Processing studies and nutrition*

The removal of colour in the recovery of sugar from cane is of industrial value and consumer importance (Kort 1979). The colour in the sugar industry results from the thermal degradation and condensation reactions of sucrose (and reducing sugars) and also from sugar-amino acid reactions via the Maillard reaction. The former reaction is also called caramelisation (Kort 1979). Various methods such as dialysis, PC etc have been used to separate the sugar colourants. They are high molecular weight compounds and their IR spectra lack sharpness of the peaks.

The mechanism of non-enzymatic browning comprises a chain of reactions involving the formation of mono- and diketosamines from glucose and glycine via the Amadori rearrangement, with subsequent degradation of the amino compounds to 3-deoxyhexosulose and unsaturated hexosuloses. The amino acids act as catalysts in the formation of carboxyl compounds as well as entering into melanodin formation. Finally highly coloured fluorescent-macromolecular pigments are formed (McWeeny *et al* 1974).

Colour development in sugar does not end with the manufacturing process but may continue during storage especially at high storage temperatures. It was shown that the colouring matter with UV absorption maxima at 285 and 280 nm was due to caramelisation products. It was proposed that 0·05% reducing sugars present in sugar crystals would undergo slow caramelisation catalysed by ash constituents, especially carbonate, during storage.

A large number of legumes and cereals have been studied for their flatus-producing property in experimental animals. This property of legumes is a constraint to their wide spread usage. Recent reports, however, claim the flatus production by starch and other unavailable carbohydrates as well (El Faki *et al* 1983a; Jaya *et al* 1979). As starch is the major carbohydrate of most of the food materials their contribution to flatulence, though small is significant. However, in an *in vivo* study it was shown that the oligosaccharide fraction (obtained from legumes) is the highest gas producer (El Faki *et al* 1983a). Hydrogen and carbon dioxide are the major gases produced. Some reports are available on the presence of large amounts of methane in flatus gas (Jaya *et al* 1979). The composition of flatus *per se* depends mainly on the nature of intestinal microflora. Generally increase in gas production occurs when the undigestible carbohydrates reach the lower intestine, where they are acted upon by the anaerobic bacteria. It is likely that the digestibility of legume carbohydrates may therefore be important in flatus production. Although flatulence is not a health problem, it is a personal-social discomfort. A close correlation between the flatus-inducing capacity and the digestibility of legumes has been made (Shurpalekar *et al* 1979). Green gram, which is more digestible produced the least amount of flatus, and Bengal gram and red gram, the least digestible, produced the maximum flatus.

From table 2 it is apparent that in comparison with legumes (table 1) cereal grains do not contain the raffinose series sugars in considerable amounts and are therefore comparatively less flatulent.

In vivo/in vitro digestibility of legume carbohydrates, viz red gram (*Cajanus cajan*), Bengal gram (*Cicer arietinum*), black gram (*Phaseolus mungo*) and green gram (*Phaseolus aureus*) in processed and unprocessed grain has been carried out (Geervani and Theophilus 1981). The processes tested were boiling, pressure cooking, roasting, germination, fermentation and parching. *Phaseolus* pulses are more digestible than other pulses. Digestibility did not improve by any of the processing methods. The increasing order of digestibility *in vivo* was red gram > Bengal gram > black gram > green gram. Significant differences in *in vivo* digestibility of moist and dry heat-treated legumes were noticed. Rats fed legume diets showed greater pH values of the contents of stomach, duodenum and small intestine than casein fed rats.

Effect of processing on flatulence-inducing capacity has also been studied. The latter increased after cooking but decreased after germination (Reddy *et al* 1980). Germination of black gram seeds for 48 h decreased the raffinose sugars but increased the content of mono- and disaccharides. Maximum hydrogen production

Table 1. Composition (%) of free sugars isolated from various legumes.

	Ground-nut[a]	Mustard[b]	Sesame[c]	Field bean[d]	Chick-pea[e]	Cow-pea[e]	Horse gram[e]	Black gram[f]	Bengal gram[f]	Green gram[f]	Red gram[f]	Winged bean[g]
Yield	9·9	12·6	11·3	7·3	7·1	8·1	3·6	2·7	6·6	4·9	6·1	3·7
Glucose	40·3	7·9	38·7	3·2	1·4	4·9	2·6	tr	1·5	8·2	1·6	36·4
Galactose	—	14·3	4·3	12·6	2·8	11·0	2·6	—	tr	—	—	45·5
Fructose	30·6	16·7	37·6	12·6	7·0	2·4	—	tr	4·5	8·2	6·5	—
Sucrose	12·5	13·5	—	28·4	16·9	11·0	21·0	18·5	21·2	20·0	21·0	9·1
Raffinose	12·5	9·5	2·1	9·5	29·6	3·6	5·3	14·8	45·5	10·2	12·9	6·1
Stachyose	—	16·7	6·5	33·1	31·0	58·5	65·8	66·7	27·3	53·1	58·1	3·0
Verbascose	2·8		4·3	tr	11·3	7·3	2·6	—	—	—	—	—
Others	1·4		6·5	0·6	—	—	—	—	—	—	—	—

Values represented on dry weight basis.
[a]Tharanathan *et al* (1975, 1976). [b]Sindhukanya and Kantharaj Urs (1983).
[c]Wankhede and Tharanathan (1976). [d]Salimath and Tharanathan (1982d).
[e]El Faki *et al* (1983c). [f]Udayasekhara Rao and Belavady (1978).
[g]Umadevi and Wankhede (1981a).

Table 2. Composition (%) of free sugars isolated from various cereals.

	Varagu[a]	Finger millet[b]	Pearl millet	Foxtail millet[b]
Yield	6·8	1·0	1·4	1·0
Glucose	35·5	9·6	12·5	11·5
Galactose	28·5	—	—	—
Fructose	8·3	13·5	11·8	10·6
Maltose	—	3·8	5·6	5·8
Sucrose	24·0	63·5	54·9	67·3
Raffinose	2·0	1·0	9·7	4·8
Stachyose	—	—	5·6	—
Others	—	—	—	—

Values represented on dry weight basis.
[a]Paramahans and Tharanathan (1980); [b]Malleshi *et al* (1986a); Wankhede *et al* (1979a); Ramachandran and Monteiro (1979).

was observed in 60% cooked black gram cotyledons. On the contrary lowering of flatus of a few legumes was noticed after cooking or germination (Reddy *et al* 1980).

Treatments such as water-soaking or sodium bicarbonate-soaking followed by cooking or autoclaving of soaked seeds or germination and/or frying of germinated seeds are commonly employed to eliminate flatus factors in legumes. These processes alter significantly, the available carbohydrate profile. Legumes, viz Rajmah (*Phaseolus vulgaris*), Bengal gram, black gram, red gram and broad bean (*Vicia faba*) on such treatments revealed a considerable decrease in the contents of total soluble sugars (which includes reducing and non-reducing sugars) and starch (Jood *et al* 1985, 1986; Iyengar and Kulkarni 1977). Losses in total soluble sugars were higher in 24 h than 48 h germinated samples. Continued (beyond 48 h) germination resulted in an increase of total soluble sugar content but simultaneously the starch content decreased. Frying also lowered the content of available carbohydrates indicating either their solubilization in the frying medium or complex formation with other components.

Some work has been carried out on the flatulence causing legumes such as red gram and kalatur (*Glycin max*) (Savitri 1986). Cooking was reported to increase slightly the content of raffinose-family oligosaccharides, whereas germination and fermentation reduced their content quite significantly (75%). After germination an increase in the contents of pentosans and hemicelluloses, but a decrease in pectin content was observed. On fermentation the non-starchy polysaccharide content decreased markedly.

From these studies it is apparent that both soaking-cooking and sprouting (for 24 h) are reasonably good treatments for reduction of flatus-producing factors as well as avoiding excessive losses of the available carbohydrate fractions.

In vitro studies, performed with a pure culture of *Clostridium perfringens* indicated that excepting cellulose, all other carbohydrate fractions were flatulent (Savitri 1986). The effect of various spices on gas formation was also tested (Savitri *et al* 1986). Gas formation was totally inhibited by raw as well as autoclaved clove, cinnamon and garlic, whereas ginger, pepper and turmeric exerted only a partial inhibition. The inhibition of gas formation was due to the inhibition of the bacterial growth except in case of garlic where some changes in the metabolic pathway was also involved. Inhibitory studies carried out with curcumin isolated from turmeric indicated that the *in vitro* effect was observed at 0·05% level of curcumin and the *in vivo* effect was at 0·05–0·5% levels (Bhavanishankar and Sreenivasamurthy 1985). Further studies employing *Escherichia coli* and intestinal microflora on the mechanism of inhibition by curcumin showed that the latter effectively chelates Fe^{3+} ions present in the diet which in turn led to the reduced activity of formic hydrogen lyase (Bhavanishankar and Sreenivasamurthy 1986), which catalyzes the conversion of formic acid into carbondioxide and hydrogen.

It was reported (Srinivasa Rao 1976) that the carbohydrates of green gram are more rapidly digested and more easily available than those of Bengal gram. The total carbohydrate content of these legumes ranged from 58–63%.

On progressive germination of bajra (*Pennisetum typhoidium*) and ragi (*Eleusine coracana*) the content of free sugars, glucose, fructose and maltose increased at the expense of starch (Malleshi 1984). During malting the content of alcohol-soluble sugars increased to ~4%. An increased level of fructose, glucose, sucrose, maltose and maltotriose was observed in the malt extract, whereas the higher oligosaccharides content decreased. Raffinose was absent in the extract.

Total carbohydrates of worts prepared from ragi-barley malt, barley malt and ragi malt were 12·5, 12·1 and 12·6 g per 100 ml, respectively. The content of fermentable carbohydrates of ragi malt was much lower (8·3) while those of ragi-barley (1 : 1) malt and barley malt worts were 10·2 and 10·0, respectively. Non-fermentable carbohydrates of ragi malt were about 50% higher than those of other two malts. All the worts contained fructose, glucose and sucrose (Venkatanarayana 1984).

From fresh ripening grains of *Sorghum vulgare* 5 fructosyl oligosaccharides were isolated and characterised (Sharma and Bhatia 1979). Three of the oligomers (F_2G, F_4G and F_9G) were found to be of the inulin-type.

The distribution pattern of sugars in 10 sorghum cultivars was examined. The free sugar content ranged from 1·3 to 5·2% and constituted predominantly sucrose together with raffinose, stachyose and small amounts of glucose and fructose (Subramanian *et al* 1980).

Malting process involves essentially a controlled germination of the grains, resulting in the elaboration of various carbohydrases with concomitant hydrolysis of seed carbohydrates. The free sugar content, increased after malting and mostly at the expense of hydrolysed starch as observed in malt carbohydrates of ragi, bajra and navane (*Setaria italica*) (Malleshi *et al* 1986a): especially, there was an increase in the level of maltose.

The quantitative changes in carbohydrates of two varieties (Red Netal and HG-4) of groundnuts (*Arachis hypogea*) during germination have been investigated (Wankhede *et al* 1977a). The content of the raffinose-series oligosaccharides decreased upto 48 h of germination and almost disappeared in the later stages of germination. Monosaccharide and sucrose contents increased considerably throughout germination. The starch content increased but the pentosan content remained constant during the initial stages of germination. The activity of α-galactosidase and lipase increased, whereas the pentosanase activity could not be detected upto 36 h of germination, but it appeared to increase afterwords.

Studies have been made on the biochemical changes in the water-soluble carbohydrates of chicory (*Chichorium intybus* Linn.) roots during development (Bhatia *et al* 1974). Sucrose, glucose, fructose and inulin-type glucofructosans were present throughout the development stage. The content of free glucose and bound fructose increased whereas bound glucose content decreased with the advancement in the growth of the roots. The ratio of bound fructose to bound glucose level increased with ageing of the roots and finally reached a maximum value. Thus, as the plant matured the content of glucofructosans increased at the expense of sucrose.

The changes in the content of sucrose, raffinose and stachyose as well as α-galactosidase present in coffee seeds of two different varieties were also investigated (Shadaksharaswamy and Ramachandra 1968a). Sucrose was the major sugar present to the extent of 90% in *arabica* extract. On soaking and germination a 50% reduction in all the sugars was noticed. Ultimately raffinose and stachyose disappeared, but traces of glucose and fructose appeared. The activity of α-galactosidse increased by 50–75% on soaking and increased further by 25% on germination of the seeds. This increase was more prominent in *arabica* than in *robusta* variety.

2.3 *Physico-chemical studies*

A study of ascorbic acid osazones by spectroscopic methods indicated that they are γ-lactones but not δ-lactones as claimed earlier (Meena Rao and Nair 1970). L-

Rhamnose-phenylosazone was found to mutarotate in DMSO solution, indicating that a C-6 hydroxyl group is not required for mutarotation (Meena Rao *et al* 1971). NMR evidence was provided for this.

The mutarotation of D-glucose was also studied after heating for different intervals of time and also after melting the sample (Nath and Singh 1969). Upto 4 h of heating (135°C) the specific rotation remained fairly constant, but after 6 h and also after melting there was a considerable drop in the rotation value and also in the ratio of α- and β-anomers (from 1 : 2 to 2 : 1). This ratio remained stable even after keeping the molten sample for 30 min, but after that it turned brown due to sugar decomposition.

Studies have been made on the kinetics of oxidation of sugars (Sen Gupta *et al* 1986; Fadnis 1986), and also on the synthesis of different sugar derivatives (Batavyal and Roy 1986; Rama Rao *et al* 1986). A variety of metal-ion oxidants such as vanadium-V, cerium-IV, manganese-III and thallium-III (Fadnis 1986) as well as halogen and their derivatives (Mishra *et al* 1986) have been widely employed in synthetic carbohydrate chemistry.

A simple colorimetric estimation based on Seliwanoff reaction has been developed for quantitative determination of sucrose in ice-cream preparations (Pantulu *et al* 1976).

The fatty acid glycoside from *Ipomoea dichroa* has been characterized to be a pentasaccharide of Glc-Fuc-Rha linked with a residue of hexadecanoic acid (Harrison *et al* 1985).

3. Water-soluble polysaccharides

Due to the presence of a large number of hydroxyl groups polysaccharides are generally hydrophilic and dissolve or disperse in aqueous medium to give solutions, sometimes forming viscous or colloidal sols. The degree of hydrophilicity of a polysaccharide, however, depends on its molecular architecture. A close and extensive hydrogen bonding may result in highly ordered regions, as in cellulose and amylose, and thus rendering such polymers insoluble or only sparingly soluble in water. Some of the linear polysaccharides are normally soluble in mild alkaline solutions; in contrast, the branched polysaccharides, such as plant exudates and seed gums, easily dissolve in water. In a sense higher the branching in a polysaccharide higher is its solubility (Smith and Montogomery 1959). Thus, in respect of solubility, the water-insoluble polysaccharides represent one end of the spectrum, while at the other end are gums such as gum arabic, mesquite, cherry, etc which dissolve readily in water giving almost true solutions. In this context it is of interest to study the cellulose-containing seed mucilages from the point of polymer-polymer interaction in terms of the solubilizing effect of the mucilaginous polysaccharides on the associated cellulose-like material.

3.1 *Chemistry and structure*

Much work has been conducted on the chemistry, structural aspects, modification and utilization of tamarind kernel powder (TKP) polysaccharides (see Srivastava 1974). The data about the composition of TKP published earlier were found to be

incorrect. Arabinose, though claimed by a few investigators (Savur 1956a), is not a true structural constituent of the polysaccharide. Three different F_1, F_2 and F_3 were extracted from the 80-mesh powder of tamarind seed meal (Savur 1956b). Unlike F_1, both F_2 and F_3 had excellent jellying and sizing properties. In particular, the work done by the scientists at the ATIRA, Ahmedabad, is noteworthy (Srivastava 1974). TKP is obtained by dry roasting, pounding and winnowing of tamarind (*Tamarindus indica*) seeds, which once upon a time was considered to be a waste byproduct of tamarind pulp industry.

TKP is essentially composed of polysaccharides together with small amounts of protein, fiber, fat, free sugars, etc. Hot water extraction of defatted TKP gave a soluble fraction (73%), which on complexing with Fehling's solution gave 3 fractions, of which fractions I and III had large amounts of protein (49 and 16%) unlike fraction II, which was almost protein-free (2·6%) (Srivastava and Krishnamurthy 1972a,b). Its molecular weight determined by osmometry and end group method was ~55,000. Fractions II and III contained glucose, galactose, xylose and arabinose in 8:4:2:1 and 4:2:1:1 ratios, respectively, indicating them to be a xyloglucan-type polysaccharide (also designated as 'amyloid' because of its I_2-positive reaction). Indeed, detailed constitutional studies (Srivastava and Singh 1967) showed fraction II to be a highly branched polysaccharide, the back bone consisting of β-D-1, 4-glucosidic linkage (as in cellulose), which is branched off at 0–6 by a side chain containing one or two sugar units of α-D-xylopyranose, β-D-galactopyranose and L-arabinofuranose. Fragmentation analysis supported the structure deduced (figure 1) (Rao and Beri 1955).

Investigations on fraction III indicated a structure similar to that of fraction II (Srivastava and Krishnamurthy 1972a,b),

Yet in another publication the polysaccharide, also called tamarind seed jellose, of TKP was reported to contain galactose, xylose and glucose (1:2:3) (Rao and Beri 1955). Acetylation of the polysaccharide gave an acetate, whose solubility was dependent on the degree of acetylation as well as of depolymerisation during acetylation. These acetates had wide melting range and were therefore useful as thermoplastic resins. Their solution in organic solvents gave fairly strong, flexible, glossy and transparent films, which adhere to glass, metallic and wooden surfaces.

A homogeneous xylan was extracted with dilute NaOH from TKP (Savur 1956c). Its M_r determined by viscosity measurements in m-cresol was 11,500 and the constitution was 50 units of β-1,4-D-xylopyranose terminated at 0–3 by one reducing and two non-reducing end groups. The xylan had a good gel-forming capacity.

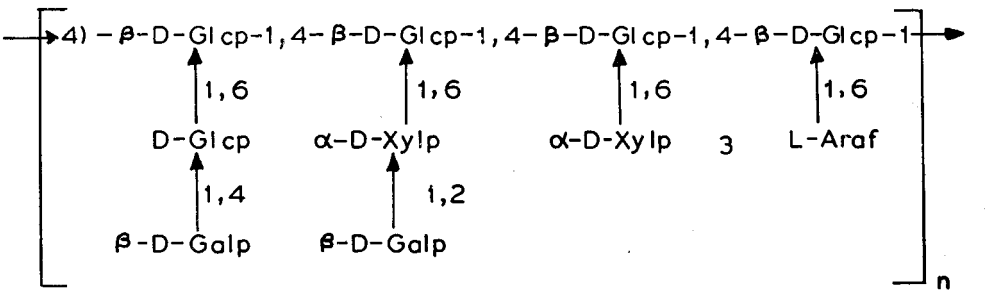


Figure 1. Structure of fraction II of TKP.

The powdered dry bark of *Cinnamomum iners* has a characteristic odour (due to cinnamaldehyde) and is used in special food preparations and also in making incense sticks, because it provides bulk and good binding properties. The latter is due to a water-soluble polysaccharide (24% yield) containing D-xylose and L-arabinose (1 : 1·45) (Pape Gowda *et al* 1980). It was found to be a branched arabinoxylan having β-1,4-linked xylose in the backbone, each of which was substituted both at 0–2 and 0–3 by L-arabinofuranose and 3-0-α-D-xylopyranosyl-L-arabinofuranose. Mild acid hydrolysis gave a degraded polysaccharide consisting mainly of xylose (90%).

From the delignified bark powder of *Persea macrantha* (family, *Lauraceae*) a water-soluble polysaccharide was extracted (28% yield) (Channe Gowda *et al* 1982). It was characterized to be a highly branched arabinoxylan (arabinose-xylose ratio of 3 : 1) with the structure comparable to that of *C. iners* polysaccharide (Pape Gowda *et al* 1980). It is speculated that the subtle variations in branching pattern of the side chain could be partly responsible for the poorer binding properties of the bark powder of *P. macrantha*. The latter property is made use of in making incense sticks.

The cold water-soluble polysaccharide of field bean (*Dolichos lablab*) husks (Salimath and Tharanathan 1982a) yielded on DEAE-cellulose (PO_4^{3-}) chromatography two homogeneous arabinogalactans (AG I in 37% and AG II in 41% yield). The molecular weight of the former was ~93,000 and that of the latter ~1,20,000. Both the fractions contained arabinose and galactose in 1 : 2 and 1 : 1·2 mol ratios, respectively. Methylation analysis of AG I revealed an average repeating unit of 30 glycoses; the backbone consisting of D-galactosyl residues mutually joined by 1,3- and 1,6-linkages, the former preponderantly in the interior and the latter mainly in exterior chains. Residues of L-arabinofuranose, and to a smaller extent L-arabinopyranose terminated some of the outer chains. It was interesting that both furanosidic and pyranosidic residues of L-arabinose were present in AG I. On the other hand, AG II had 1,6-linked backbone of D-galactose with branch points at 0–3 of doubly substituted residues of L-arabinose.

From *Dillenia indica* fruits an L-arabino-D-galactan was isolated in 2% yield. Based on partial acid hydrolysis data and methylation analysis the polysaccharide was found to be a 1,4-β-D-galactan possessing L-arabinofuranose side chains linked at 0–3 of some of the D-galactose residues (Srivastava and Pande 1978).

A new affinity matrix has been prepared by cross-linking of larch arabinogalactan with epichlorohydrin. This matrix has strong affinity, greater than any other matrix investigated so far, for the *Ricinus communis* lectin (Majumdar and Surolia 1978).

From immature pods of *D. lablab* a homogeneous D-galactan was isolated by hot water extraction of the chlorophyll-free pods and subsequent fractionation as calcium chloride complex (of the acidic polysaccharide) and by DEAE-cellulose (PO_4^{3-}) chromatography. Structure analysis showed the galactan to have a β-1,4-linked core with side chain branches at 0–6 of a few of galactosyl residues (Ghosh and Das 1984).

Repeated aqueous extractions of alcohol-insoluble residue from defatted mustard (*Brassica juncea* var. *varuna*) seed meal furnished a crude polysaccharide, which after purification yielded a polysaccharide exclusively composed of L-arabinose (Tharanathan *et al* 1985). From the results of methylation analysis the molecule appeared to be an arabinan having a highly substituted (at 0–2/0–3)1,5-linked arabinosyl backbone. The presence of L-arabinopyranose in mustard seed is unusual.

An arabinan having similar structural features as above, was recently reported in cowpea (*Vigna sinensis*) endosperm (Muralikrishna and Tharanathan 1986). The arabinan was isolated by 10% TCA extraction at 4°C for 4–6 h and successive fractionation on DEAE-cellulose (CO_3^{2-}). The homogeneous arabinan had M_r ~11,600. Both these arabinans, in all possibility, appeared to be non-degraded polysaccharides, as the isolation procedures employed were mild. The possibility that cowpea arabinan may be a degradation product derived during TCA extraction step was ruled out by the observation that commercial pectin (from citrus) and arabinogalactan (from larch wood) on similar treatment with 10% TCA (4°C for 6 h) did not show any detectable degradation products in the extract.

The flowers of mahua (*Madhuca indica*) constitute a rich source of sugars and are used traditionally as cooling agents, and as a tonic for alleviating coughs and bronchitis. Aqueous extracts of the flowers contain a crude polysaccharide, which on Sephadex G-150 chromatography was resolved into two homogeneous fractions (Sarkar and Chatterjee 1983). One of them was composed of D-galactose, L-arabinose, L-rhamnose, D-xylose and D-glucuronic acid (21 : 5 : 1 : 1 : 6). The polysaccharide was found to possess a 1,3 linked D-galactan backbone having side chain terminals at 0–3, 0–4 and 0–6; the rhamnose was 1,2-linked.

Aqueous extraction of defatted cashewnut meal furnished a polysaccharide which was characterized by fragmentation analysis. Mild hydrolysis of the polysaccharide with 0·01 N H_2SO_4 yielded a few neutral oligosaccharides (Bose and Soni 1971, 1972) and a degraded polysaccharide. The latter by methylation experiments was established to be a branched 1,3- and 1,6-linked D-galactan having side chains of D-galactose and 6–0-(β-D-galactopyranosyluronic acid)-D-galactopyranose (Bose and Soni 1973, 1974). This oligosaccharide was also obtained by graded hydrolysis of the degraded polysaccharide. The partial hydrolyzate consisted of galactobiose, galactotriose and two partially identified galactotetroses having 1,3- and 1,6-linkages (Bose and Soni 1971).

Hot water extracts of the fresh leaves of *Aloe barbadensis* Miller yields a mixture of polysaccharides containing pectic acid together with a galactan, a glucomannan and an arabinan (Mandal and Das 1980). Removal of pectic acid by complexing with calcium chloride followed by DEAE-cellulose fractionation gave a galactan possessing 1,4-linkage with occasional branches at 0–6.

A water-soluble fructosan has been isolated from the stems of *Agave vera cruz* Mill. and characterized (Srinivasan and Bhatia 1953). The aqueous extract also contained free glucose and fructose. The distribution of fructosan, however, was not uniform along the length of the stem; there was a carbohydrate gradient all along (Srinivasan and Bhatia 1954). The fructosan was highly branched with 2,1- and 2,6-linked β-D-fructofuranose residues terminated by a non-reducing D-glucopyranose.

Polyfructosans have also been identified in *Furcraea gigantea* Vent. which was purified by acetylation followed by deacetylation (Bhatia and Srinivasan 1953).

Hot water extraction of defatted garlic bulbs (*Allium sativum* Linn) (Nath and Das 1978) and onion (*Allium cepa* Linn) (Sen *et al* 1971) yielded a mixture of polysaccharides of D-galactan, D-galacturonan, L-arabinan and L-fructan-types. L-Fructan is a reserve carbohydrate in *Agave* (Srinivasan and Bhatia 1953). The polysaccharide was shown to be a 2,1-linked fructan having occasional D-glucopyranose residues. By fractional precipitation and DEAE-cellulose chromatography a homogeneous galactan was obtained with 1,4-linked galactose in the backbone and having branches at 0–6 of some of the galactose residues. The

pectic fraction of onion (Sen *et al* 1971) on treatment with polygalacturonase followed by 70% alcohol extraction furnished a pure 1,4-galactan having some amount of branching at 0–6.

The polysaccharides of the seeds of *Anthocephalus indicus* A. Rich contain D-xylose, D-mannose and D-galactose in 1:3:5 mol ratio (Gupta 1980). Constitutionally it was found to be a linear molecule of 1,4-linked β-D-mannopyranosyl and β-D-glucosyl residues to which were attached residues of α-D-xylose and β-D-glucose in 1,6-linkages.

The cotyledon of *Mirabilis jalapa* seeds is known to contain considerable amounts of a protein-free polysaccharide (Ghosh and Rao 1981). The seeds find use in Indian medicine for curing syphilitic sores subduing inflammation and also as a purgative. The water-extractable glucan present in the seeds was mainly 1,4-glycosidically linked, with a few 1,3-links in between (Ghosh and Rao 1981). At branch points glucose was linked through 0–2 and 0–4. Occasionally a sequence of contiguous 1,3-linked glucose residues was also noticed. Interestingly, both α-and β-D-glucosidic linkages were present, the former being preponderant. They were identified by their characteristic IR bands at 850 and 890 cm^{-1}, respectively. The bands at 850 and 925 cm^{-1} were characteristic of 1,4-α-glucans and the broad band at 1630 cm^{-1} was due to bound water. The glucan gave a faint blue colour with I_2 having an absorption maximum of 420 nm.

The seeds of *Pheonix dactylifera* have medicinal values used for headache and hermicarnia. Preliminary studies on the water-soluble polysaccharide indicated the presence of mannose and galactose (12:1) (Jindal and Mukherjee 1969).

An arabinoglucan (D-glucose: D-arabinose in 21:4 ratio) was isolated from the fruits of *Cordia dichotoma* Forst. which was purified by gel permeation chromatography (Basu *et al* 1984). The polysaccharide with an average DP of 144, on detailed studies was found to have a backbone of 1,6-linked glucopyranosyl and 1,2-linked arabinofuranosyl residues.

From the seeds of *Cassia multijuga* (Dubey and Gupta 1979), new water-soluble polysaccharide composed of D-galactose, D-mannose and D-xylose (5:1:2) was isolated. Methylation and oxidation experiments revealed 2,3-Me_2-galactose, 2,3,6-Me_3-galactose, 2,3,4,6-Me_4-galactose, 2,3-Me_2-mannose, 2-Me-xylose, 2,3-Me_2-xylose and 2,3,4-Me_3-xylose in 2:4:4:2:1:2:1 mol ratio, respectively. Oligosaccharide characterization (Gal-1$\xrightarrow{\alpha}$6-Gal; Man-1$\xrightarrow{\alpha}$6-Gal; Xyl-1$\xrightarrow{\beta}$4-Gal; and Xyl-1$\xrightarrow{\beta}$3-Xyl) lent support for the structure deduced.

The nature of carbohydrates in the water-soluble extracts of different forage plants was studied. Limited distribution of fructan was recorded in the leaves and stem of these tropical plants.

Polysaccharides from raw coffee seeds (*Coffee arabica*) were shown to be arabinogalactans containing small amounts of galacturonic acid (Shadaksharaswamy and Ramachandra 1968b).

The polysaccharide, isolated from the pods of *Opuntia dillenii* was composed of L-arabinose and D-galactose (1:3). Structurally, it had interior chains of β-1,4-linked D-galactopyranose units to which were attached non-reducing L-arabinofuranose residues at 0–3. A small number of D-galactopyranose side chains were also found attached at 0–3 of some residues in the main chain.

3.2 *Biochemistry*

In *Agave* a transfructosidase was identified (Bhatia *et al* 1955a): it had a pH optimum of 5·6–5·8 and a maximum activity at 37°C. The enzyme mediated the synthesis of polyfructosan from sucrose. The enzyme was specific for the transfer of fructose residue, present in an unsubstituted form as in sucrose or raffinose, but not melizitose or planteose (Satyanarayana 1976a, b). It seemed to bring about the formation of 2,1-linkage, and specifically synthesised only one trisaccharide, 1-kestose from sucrose, which may have a bearing on the fructan biosynthesis (Satyanarayana 1976c). Its M_r was 62,000.

$$\underset{\text{sucrose}}{\text{F-G+F-G}} \xrightleftharpoons{\text{Enzyme I}} \underset{\text{oligosaccharide}}{\text{F}_2\text{G}} + \underset{\text{glucose.}}{\text{G}}$$

In addition to this, a few other associated enzymes (II and III) are also involved in the biosynthesis of various fructose-containing oligosaccharides (of DP 3–8) occuring in the plant (Satyanarayana 1976b).

$$\text{F}_2\text{G}+\text{F}_2\text{G} \xrightarrow{\text{Enzyme II}} \text{F}_3\text{G}+\text{FG}$$

$$\text{F}_2\text{G}+\text{F}_2\text{G} \xrightarrow{\text{Enzyme III}} \text{F}_4\text{G}+\text{F}_2\text{G}$$

$$\text{F}_3\text{G}+\text{F}_3\text{G} \longrightarrow \text{F}_3\text{GF}+\text{F}_2\text{G}.$$

Basic structures of these (homologous) oligosaccharides were established by methylation followed by GLC-MS and [^{1}H]-NMR analyses (Dorland *et al* 1977). These oligomers seemed to be necessary intermediates in fructan synthesis. Sucrose played a dual role both in the initiation and elongation of the fructan chain, as shown by the incorporation of [U-^{14}C]-sucrose leading to [U-^{14}C]-fructose followed by a polymer-like compound (Satyanarayana 1976c).

On the contrary, the transfructosidase obtained from *Polianthes tuberosa* Linn. had slightly different characteristics with temperature optimum of 25°C. This enzyme is more thermolabile (inactive at 45°C) than the one from *Agave* (inactive at 55°C) (Bhatia and Srinivasan 1954).

The carbohydrase fraction of garlic was shown to contain invertase and polyfructosidase (Bhatia *et al* 1955a). Unlike in *Agave* no definite evidence was obtained for the presence of transfructosidase in garlic.

The *in vivo* biosynthesis of D-gluco-D-fructosans by the D-fructosyltransferase of *Agave americana* has been accomplished (Nandra and Bhatia 1980). Scurose was the substrate used and oligosaccharides up to DP of 10 D-fructose residues could be obtained. None of these oligosaccharides could serve as substrates. Whereas the D-fructosyltransferase, obtained from *Fusarium oxysporum* and purified by conventional techniques, produced a series of low M_r products (Gupta and Bhatia 1980).

3.3 *Modification*

By chemical and enzymatic treatments low viscosity TKP (LTKP) was prepared, which had viscosity comparable to that of hydrolysed starch and having a low

degree of set back (Srivastava *et al* 1970b). LTKP of different grades have a wide range of intrinsic adhesive strength of use in textile industries. Moisture regain of LTKP-sized yarns was considerably more than yarns sized with starch. Desizing, bleaching and dyeing of LTKP-sized fabrics were easy.

Dextrinization (by heating with 0·074% HCl at 153°C for 5 h) of TKP gave a product which on fractionation gave a homogeneous polysaccharide possessing a structure devoid of a few side chain stubs (figure 2) (Srivastava and Krishnamurthy 1972b).

Oxidation of tamarind seed polysaccharide (TSP) with a mixture of DMSO-acetic anhydride [a reagent used for specific oxidation of isolated secondary hydroxyl groups (Lindberg 1972)] followed by conversion of one portion into alcohols by borohydride reduction and the other portion into aminodeoxy derivative by treating with hydroxylamine hydrochloride (to form the oxime) followed by reduction with $LiAlH_4$, offered a convenient route for the synthesis of 2-amino sugars, which are of biochemical interest due to their wide natural occurrence. Here the oxidation takes place preferentially at C-2.

3.4 *Application*

In consonance with its highly branched structure TKP gives pastes of high viscosity at low concentration, which do not retrograde. α-and β-amylases have no action on TKP, whereas cellulase degraded the molecule, reducing its paste viscosity (Srivastava 1974).

Extensive laboratory and mill trials showed that TKP could successfully be used as cotton warp sizing agent (Srivastava 1974). In spite of a few drawbacks such as its high viscosity at low concentration and the difficulty in completely removing the size during desizing operations, which resulted in poor bleaching and dyeing characteristics, TKP was superior to starch as a size due to the excellent storage stability of its paste and economy in the usage of softener. The presence of fatty material (5–7%) in TKP acted as a softener.

The stem juice of *Agave* is utilized by the honey bee, and as a replacement of non-leafy vegetable (Bhatia and Pingale 1954). Due to its high calcium content it also has a supplementary value to the rice diet. It is a useful raw material for the preparation of fructose syrups. Conditions for the preparation of fructose syrup from this source were standardized (Srinivasan *et al* 1963) and the method consisted of acid hydrolysis of a concentrated water extract of dressed and sliced stem, neutralization

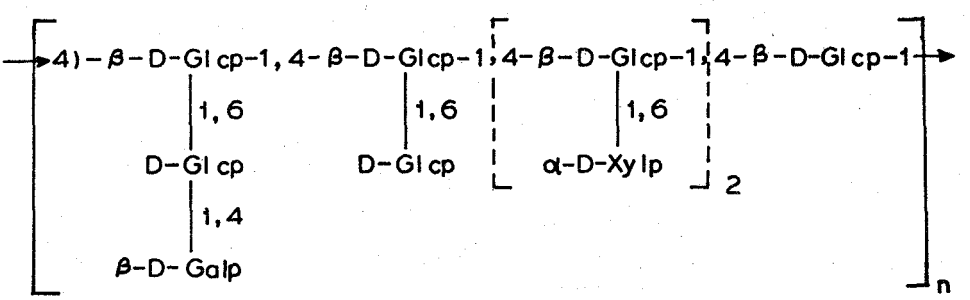


Figure 2. Structure of dextrinized TKP.

with lime, filtration, decolourization and vacuum concentration to 70–80% of solids. The latter contained 90% fructose and 10% glucose.

The syrup had a sweet and pleasant taste, was golden-yellow in colour and showed no deleterious effects as revealed by rat-growth studies wherein the starch diet (control) was replaced by 25–50% with the high-fructose syrup (Srinivasan *et al* 1963).

4. Starch

Many edible and non-edible sources have been utilized for the isolation of starches of differing physico-chemical characteristics. Such variations in the properties may exist because of differences in plant species, agronomic conditions and gene mutations. These differences could also be representative of varied stages of starch biosynthesis, as it is known that a plant is not a static biosynthetic entity.

4.1 *Legume starches*

4.1a *Physico-chemical studies*: Starch is the major carbohydrate in most of legume seeds and it represents nearly 25–40% (w/w) of the seed (dry weight). Its extraction is fairly easy and is normally done by the water steeping method. The crude starch is purified by treatments with mild alkali (to pH 8–9) and sodium chloride-toluene (10 : 1, v/v). These remove the protein(s) to a considerable extent to yield pure white starch (Schoch 1964). Majority of the legume starches are non-ionic in nature and differ in shape and size (table 3) and exhibit single-stage swelling. All of them show characteristic polarization crosses when viewed in polarized light.

From two varieties (Red Netal and HG-4) groundnut starch was isolated in 13 and 18·2% yields, respectively (Wankhede *et al* 1977b). The granules varied in their shape and size (table 3). The starch was found to be contaminated with protein (3%), probably due to the presence of finely hydrated fiber fraction; and the total lipids (0·5 and 0·6% respectively for the 2 varieties), which significantly varied in palmitic and oleic acid contents. Gross variations were also noticed in the range of their gelatini-

Table 3. Physico-chemical characteristics of legume starch granules.

Source	Shape	Size (μm)	Protein (%)	Amylose (%)	Amylopectin (%)	GT range (°C)
Groundnut[a]	Round	5–30	2·8	30	70	62–71
Field bean[b]	Round-oval	10–30	0·2	ND	ND	ND
Black gram[c]	Round-oval	10–12	0·9	32	69	ND
Horse gram[d]	Oval	15–85	0·5	34	66	71–80
Chick pea[e]	Oval	8–54	0·7	32	68	60–75
Cowpea[f]	Oval	4–39	0·5	33	67	65–73
Mango kernel[g]	Round	4–5	ND	ND	ND	79–80
Great northern bean[h]	Round	12–40	ND	10	90	ND
Winged bean[i]	Oval	20–35	1·8	37	63	61–70

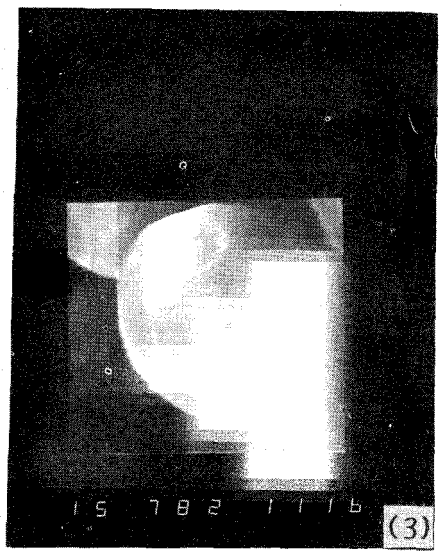
ND, Not determined.

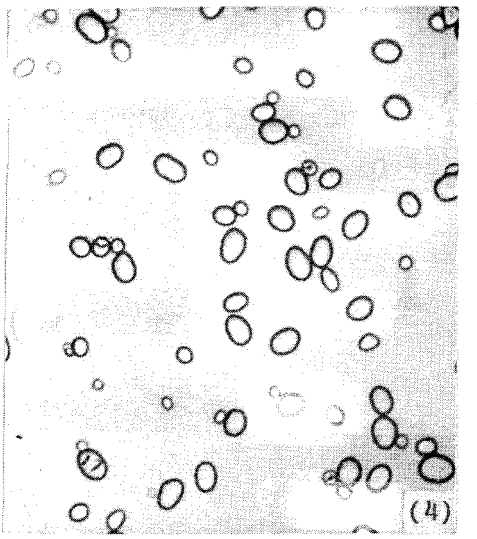
[a]Wankhede *et al* 1977b; [b]Salimath and Tharanathan 1982d; [c]Sathe *et al* 1982; [d–f]El Faki *et al* 1983b; [g]Srivastava *et al* 1967; [h]Sathe and Salunkhe 1981; [i]Umadevi and Wankhede 1981b.

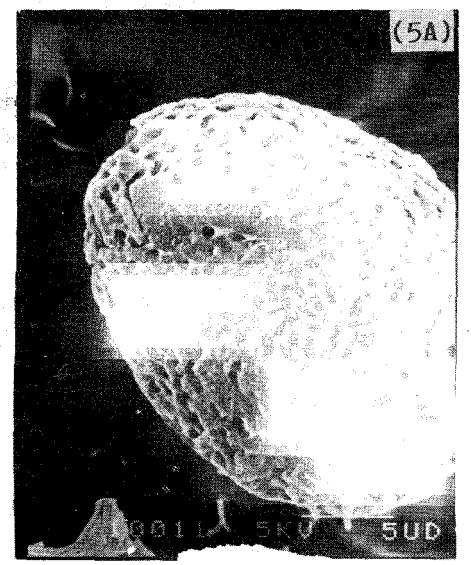
zation temperatures (GT), as well as in solubility (in water and DMSO) and swelling behaviours. The amylose fraction exhibited a higher β-amylolysis limit (Aspinall 1970a). In SEM the amylase-digested starch granules showed considerable erosion of the surface (figure 3) (Tharanathan *et al* 1980).

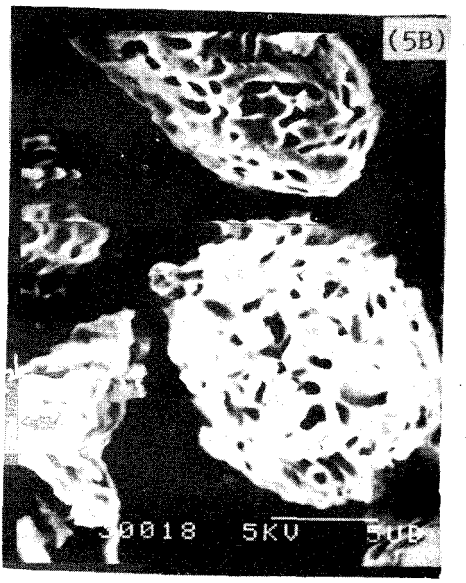
Report of a very high content of starch (34·5%) in winged bean (*Phosphocarpus tetragonolobus*), of high proportion of amylose (38%) and of the digestibility with glucoamylase (at 37°C) (Umadevi and Wankhede 1981b) need to be confirmed.

From great northern bean (*Phaseolus vulgaris* L.) starch was isolated in 18% yield.









Figures 3–5. 3. SEM of groundnut starch granules attacked *in vitro* by salivary α-amylase. 4. Photomicrograph of chick pea starch granules under ordinary light, indicates mixed granule population. 5. **a.** SEM of *in vivo* digested cowpea starch granules isolated from caecum. **b.** SEM of *in vivo* digested horse gram starch granules isolated ffrom caecum.

The starch contained 10·2% amylose and showed restricted swelling in Brabender amylograph (Sathe and Salunkhe 1981). At room temperature the starch had good water and oil adsorption capacities and at 7% and above it formed a stable gel (Sathe and Salunkhe 1981).

Some physicochemical characteristics of moth bean (*Phaseolus aconitifolius*) starch have been reported (Wankhede and Ramteke 1982). The starch yield was 33·5%. Its GT was 67–72°C and it showed single stage swelling. The starch was easily soluble in DMSO, indicating heterogeneous bonding forces. The starch was non-ionic and had an amylose content of 26·4%. Galatinized starch exhibited better amylolytic digestibility compared to native starch.

Recently starches were isolated from cowpea, chick pea (*Cicer arietinum*) and horse gram (*Dolichos biflorus*) and partially characterized (El Faki *et al* 1983b). The starch yield varied from 28–37% and all of them showed mixed granule population (see table 3, figure 4). To some extent these starches varied in their swelling and solubility behaviour, cowpea and horse gram starches were more soluble in DMSO. In alkaline solution all the starches exhibited high viscosities. Compared to the other two starches, chick pea starch had low slurry and low set back viscosities in Brabender amylograms. X-ray diffraction patterns revealed cowpea starch to be of A-type and chick pea and horse gram starches to be of B-type.

Preliminary studies were reported on the starch isolated (45% yield) from black gram (*Phaseolus mungo*) *dhal* (Sathe *et al* 1982). The granules were of different shapes and sizes (7·5–28·5 μm in length, 7·5–27 μm in width). The starch had an amylose content of 26%, and a very narrow range of GT 71·5–74%. The raw as well as the cooked black gram starch was resistant to *in vitro* amylolysis with hog pancreatic α-amylase.

Starch has been isolated (60–70%) from mango (*Mangifera indica*) kernel seed, which is considered to be a waste byproduct. As an alternative to corn starch, which is the principal starch of commerce, mango seed starch has tremendous potential for further exploitation (Srivastava *et al* 1967).

From banana psuedo-stem (*Musa paradisiaca* Linn. and *M. sapientum* Linn.) starch was recovered in 2–5% yield: potassium metabisulfite was added during starch isolation, to inhibit browning (Patil and Magar 1974). The isolated starch had an amylose content of ~20% and a high intrinsic viscosity (Subrahmanyam *et al* 1957; Shantha and Siddappa 1970a). The latter was attributed to its high M_r. The *in vitro* digestibility of banana stem starch was almost parallel to that of maize starch (Murthy and Swaminathan 1953). A quick method consisting of determining the capillary flow time of aqueous NaOH solution of banana starch was also developed (Jain *et al* 1956). In another study it was shown that there existed variation in the content of starch, which depends on the variety, locality, maturity and the physiological state of the plant and also on the agronomic (climate, moisture, etc) conditions (Subrahmanyam *et al* 1957). The concentration of starch was higher in the middle fleshy leaf sheaths and increases gradually towards the rhizome downward along the length of the pseudo-stem. Because of the difficulties in the starch extraction after the inflorescence period, the pseudo-stem was utilized soon after the harvest of the bunch for starch isolation (Shantha and Siddappa 1970b). The banana pseudo-stem is otherwise a waste material after the fruit is harvested and therefore offers a useful source of additional starch to meet the cereal food shortage.

Starch has been isolated from Bengal gram (*Cicer arietinum*), a pulse grain

(Srivastava *et al* 1970a). Preliminary coarse grinding and winnowing was necessary to separate the seed kernels from the testa. From the kernels starch was isolated by steeping with sulphur dioxide, grinding and centrifugation. The recovered starch granules were of different shapes (round, egg shaped and triangular), and some granules had high striations. On Brabender amylograms the starch showed very low peak viscosity as well as set back viscosity.

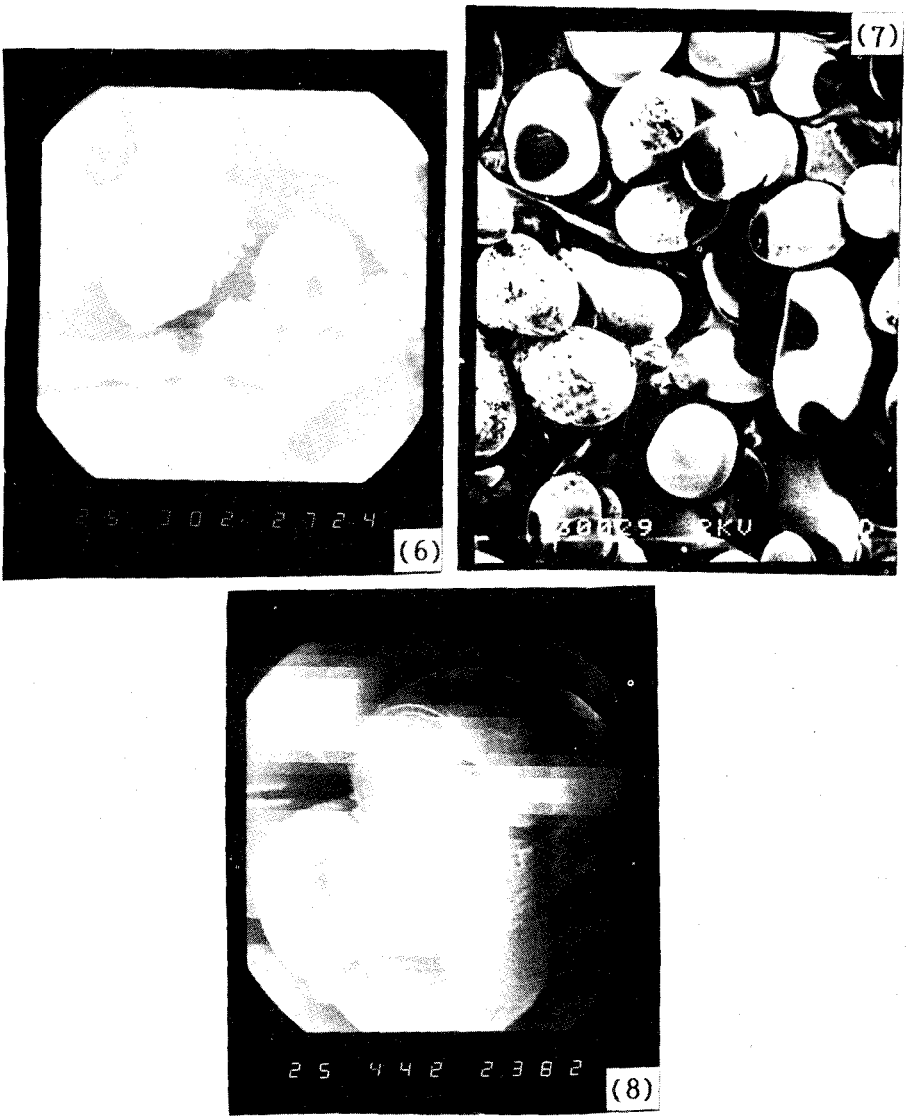
From the seed polysaccharides of *Pongamia glabra* Vent. a mixture of starch-protein in 55:45 ratio was obtained (Harshe and Srivastava 1969). Failure to dissociate these components indicated it to be a covalent complex.

4.1b *In vivo and in vitro experiments*: Preliminary results of *in vivo* and *in vitro* studies indicated the influence of starch (and hemicellulose) on the total flatulence caused by chick pea, cowpea and horse gram (El Faki *et al* 1983a). Unlike the free oligosaccharides of raffinose-series, which are easily removable by 70% alcohol extraction, the removal of starch was found impractical as it was the major component of the legumes. Of the various processing methods employed to eliminate flatus-causing factors, a wet method involving extraction of the legume flour with water (to remove soluble carbohydrates) followed by sieving of the aqueous slurry through 200-mesh to remove a major portion of the hemicellulose/cellulose was found satisfactory. This method gave a product with minimum flatus inducing effect. In a further study (El Faki *et al* 1984) it was observed that while the endosperm carbohydrate fractions caused flatulence, the husk and the derived carbohydrate fractions were inhibitory to gas formation by *Clostridium perfringens*. This inhibitory effect was attributed to the presence in the seed coat of phytates and/or phenolic acids (El Faki *et al* 1984).

The *in vivo* digestibility of these starches was lower than that of corn starch (El Faki *et al* 1983d). Significant differences in the weights and contents of small intestine and caecum of rats were noticeable between the control and the experimental groups. The caecum pH of rats fed legume starches was distinctly acidic in comparison with that of rats fed corn starch, which was neutral. The former could be related to the formation of carbon dioxide and organic acids as a result of fermentation of indigestible carbohydrates. The data obtained from SEM studies (El Faki *et al* 1983c) indicated that among the granules isolated from stomach, chick pea starch appeared to be digested better.

Starch granules from horse gram and cowpea were attacked *in vivo* to a very little extent. In addition to the enzymes the acidic pH in the stomach also contributes to the morphological changes of the granules. In the small intestine the above starches appear to be digested well as revealed by their morphological aberrations. However, in the caecum as well as in the large intestine significant erosion of the granules was visible. The attack was more pronounced in horse gram and cowpea starch granules (figures 5a,b) wherein there was extensive pitting all over the granule surface, which had penetrated deeper into the granules at many locations. In figure 6a tunnelling attack on one of the chick pea granules was visible.

Considerable differences were discernible in the kinetics of amylolysis in *in vitro* digestibility (El Faki *et al* 1983d). With comparable enzyme-substrate ratio, glucoamylase showed a better amylolysis than salivary α-amylase. Chick pea starch appeared to be the best substrate for amylolysis. In addition to surface erosion and as a result of surface roughness, some granules possessed hollow curvatures.



Figures 6–8. **6.** SEM of *in vivo* digested chick pea starch granules isolated from large intestine, indicates a tunnelling attack on one of the granules. **7.** SEM of horse gram starch granules attacked by glucoamylase. **8.** SEM of field bean starch granules attacked by glucoamylase.

Particularly the SEM of horse gram starch granules was interesting because of the divergent nature of enzyme attack. Here, some granules possessed wide punctures and looked 'bowl' shaped, while some others had characteristic enzyme pitting and surface layering (figure 7). The double or multiple hollow depressions on the same granule appeared quite unusual. Some variations were also observed in the mode of enzyme attack between the small and the large lenticular granules.

Some studies have been made on field bean starch (Salimath and Tharanathan 1982d). Significant amylolysis of native starch granules occurred when incubated

with glucoamylase. The enzyme-attacked granules had characteristic onion-type layering (figure 8). Looking at the kinetics of amylolysis it appears that the enzyme preparation is possibly contaminated with some α-amylase.

As regards the *in vitro* starch digestibility no large differences were noticed among *desi* and *kabuli* cultivars of chick pea (Singh *et al* 1982). Cooking, prior to amylolysis, considerbly increased the digestibility of chick pea, cowpea and green gram (Shurpalekar *et al* 1979). Pre-treatment with HCl-pepsin markedly enhanced the digestibility of uncooked legumes. Among the 3 legumes, green gram starch showed a slightly higher digestibility, both in the cooked or uncooked form.

4.1c *Processing studies*: Some studies were also conducted on a few functional characteristics such as the cooking and eating qualities of chick pea (Narasimhan 1984). It was found that the isolated starch from good-cooking varieties hydrated faster than those from poor-cooking varieties. The two starches also showed differences in amylose content and in their gel chromatographic profiles. It was reported that the pectins have an inverse relationship in reducing the swelling and solubility behaviour of pulse starch (Narasimhan 1984). Setting properties of legume starches have been related to the ratio of amylose and amylopectin components (Radley 1976).

4.2 *Cereal and millet starches*

4.2a *Physico-chemical studies*: Cereals and millets are the basic staple food materials of a great majority of population in India. They are grown particularly in many areas of Asia, Africa and Latin America. Both cereals and millets are mainly starchy foods (table 4) excepting a few such as proso (*Panicum miliceum*) and foxtail (*Setaria italica*) millets, which are reported to be high in protein, ash and fiber contents (Matz 1959).

Previous defatting was found necessary (Shanthy *et al* 1980) for accurate determination of amylose in rice starch. The content of water-insoluble amylose correlated well with the pasting behaviour and textural attributes of rice varieties (Shanthy *et al* 1980). Studies on fractionation of starch from different rice varieties by gel permeation techniques showed that the separated amylopectin fraction (eluting in the void volume) stains blue with iodine. The absorption maxima of the blue colour varied among the varieties, and this had a good correlation with the properties of the starch (Bhattacharya and Chinnaswamy 1986).

The total carbohydrate and starch contents of several red rice varieties were found to be low as compared to conventional white varieties (Srinivasa Rao 1976a). The starch content of red rice ranged from 54–68% as against 59–76% in the white varieties. The soluble sugars however constituted 1–2% in both the varieties. The *in vitro* digestibility test indicated little difference between these varieties. Excepting a few which had low amylose values (17%) the majority of other varieties had an amylose content similar to that seen in conventional white varieties (18–20%). The results in general indicated red rice varieties to have relatively lower amounts of available carbohydrates and that they are more slowly digestible as assessed by *in vitro* α-amylolysis.

Some studies have also been made on the nature of carbohydrate moiety in high yielding varieties of rice (Srinivasa Rao 1970). Amylose content in these rice starches

Table 4. Physico-chemical characteristics of cereal/millet starch granules.

Source	Shape	Size (μm)	Protein (%)	Amylose (%)	Amylo-pectin (%)	GT range (°C)	References
Rice	Round	3–5	0·1	25	75	68–72	Srinivasa Rao (1976)
Ragi	Round-polygonal	5–15	1·2	18	82	65–68	Wankhede *et al* (1979)
Navane	Round-polygonal	5–25	1·4	19	81	55–62	Wankhede *et al* (1979)
Bajra	Polygonal	4–22	1·0	38	62	62–74	Malleshi (1984)
Sorghum	Round	4–25	0·4	35	65	66–76	Arora and Luthra (1972)
Varagu	Round-polygonal	7–15	0·2	24	72	57–68	Paramahans and Tharanathan (1980)
Panivaragu	Round-polygonal	1·5–18	5·5	25	76	68–76	Muralikrishna *et al* (1982)
Samai	Round-polygonal	1·5–18	3·3	18	82	55–72	Muralikrishna *et al* (1982)
Sanwa	Round-polygonal	2·5–20	4·1	20	80	50–70	Muralikrishna *et al* (1982)

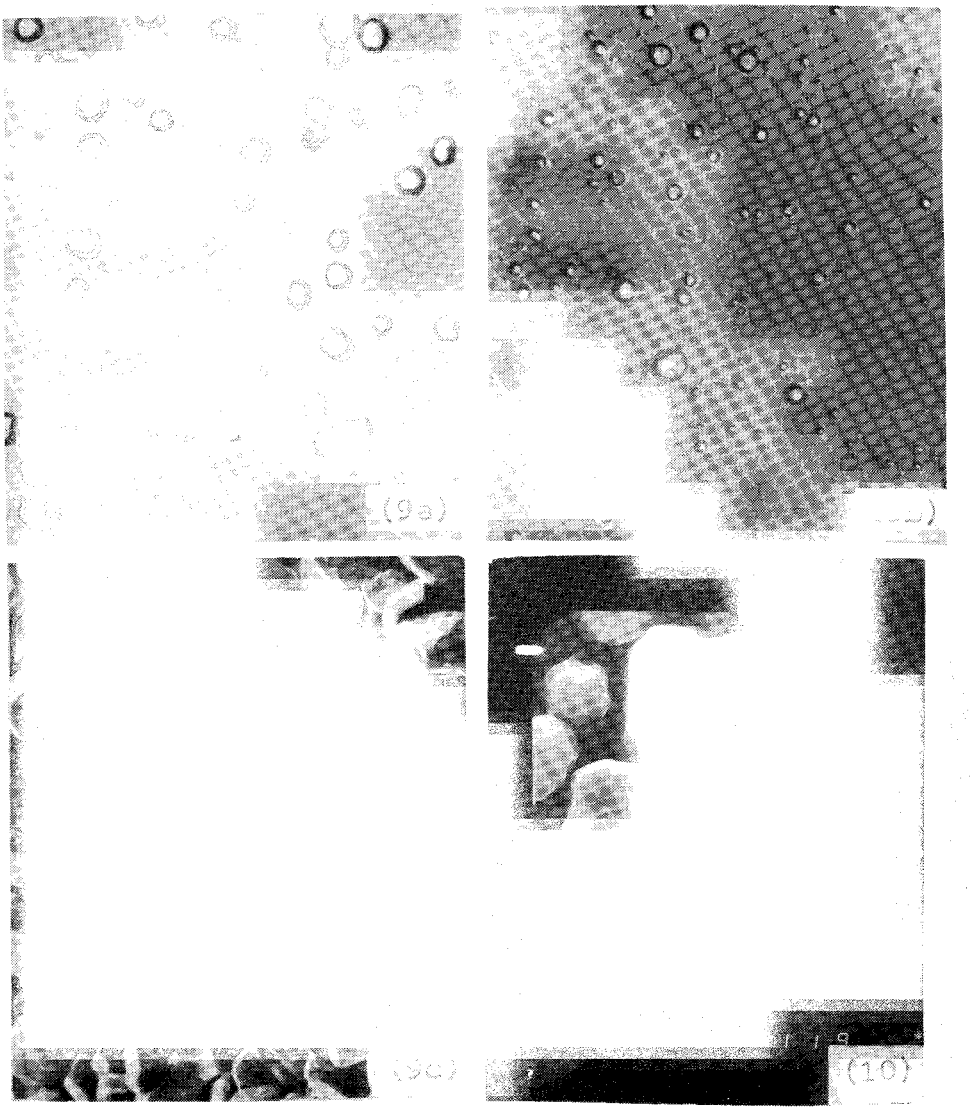
varied from 15–22%. The *in vitro* digestibility trials carried out with pancreatic α-amylase indicated the Hamsa variety to be much more susceptible to α-amylolysis than any other variety analysed so far. This was also reflected in the relatively higher peak values for blood sugar in 5 out of 8 cases studied. The Hamsa variety was also found preferable for its cooking quality.

Strong bonding forces between the linear and the branched molecules as well as the overall starch granular nature and its structure also result in poor retrogradation. Difference in the degree of retrogradation is also dependent on the qualitative-quantitative nature of the constituent amylose.

Starches isolated from a wide variety of millet grains were studied. The millets used were finger millet (ragi) (Wankhede *et al* 1979b), foxtail millet (navane) (Wankhede *et al* 1979b), varagu (*Paspalum scrobiculatum*) (Paramahans and Tharanathan 1980), samai (*Panicum miliare*) (Muralikrishna *et al* 1982), sanwa (*Echinochloa frumentaceae*) (Muralikrishna *et al* 1982) and proso millet (panivaragu, *Panicum miliceum*) (Muralikrishna *et al* 1982). There were subtle variations in M_r and chain length of starch components (amylose/amylopectin). But no significant differences were discernible in several other physico-chemical properties such as peak viscosity in Brabender amylograms, the solubility and swelling behaviour in water and DMSO, and the presence of various non-starch polysaccharides in the respective millets. All the starches had very high solubilities in DMSO, indicating easy penetration of the solvent into the strongly bonded miscellar granule structure.

Amylose content of these starches ranged from 14–21%. Unusually ragi was reported to contain a low proportion of amylose (Wankhede *et al* 1979b). Differences were also seen in their range of GT (see table 4) and also in the presence of other non-starch constituents. Such variations in GT, and in turn the rate of swelling, are the result of granule size distribution and heterogeneous nature of bonding forces within the granules. A higher GT range and consequently poor degree of swelling power indicated a tightly associated granule.

All starches possessed mixed granule populations of different shapes and sizes, ranging from small spherical granules to big hexa-polygonal granules (see figures 9a, b, c). The small granules exhibited very poor birefringence characteristics for



Figures 9–10. **9.** Photomicrograph of samai starch granules under ordinary light indicates **a.** big-hexagonal granules **b.** small spherical granules and **c.** SEM of ragi starch granules. **10.** SEM of varagu starch granules, indicates scars on the granules.

reasons unknown. A gross separation of the various granule populations was achieved by treatment with mild alkali (pH 8 for 5–10 min at room temperature) followed by successive decantations and high-speed centrifugation (Muralikrishna *et al* 1982). In the case of wheat starch it has been claimed that the pasting characteristics, differences in the digestibility, and the content of amylose, all depend on the interactions between different sized granules (Meredith 1981). In comparison to corn starch the millet starches had a higher intrinsic and inherent viscosity in alkaline solutions.

By repeated purification the protein content of varagu starch could be brought down to as low as 0·24% (Paramahans and Tharanathan 1980). On the other hand sanwa, samai and panivaragu starches had high protein contents (3·3–5·5%) in spite of repeated purifications (Muralikrishna *et al* 1982). This was akin to legume starches which normally had high protein contents (El Faki *et al* 1983b). The presence of high amounts of protein (together with lipids) confers resistance to mechanical damage on the granular surface, and possibly also towards amylolysis.

Like other cereal starches the total lipid content of ragi (Wankhede *et al* 1979b), navane (Wankhede *et al* 1979b) and varagu (Paramahans and Tharanathan 1980) starches ranged between 0·8–1·6%. Although qualitatively similar, considerable differences were discernible in their quantitative makeup. In the free and bound lipid fractions of ragi and varagu, palmitic acid (C16:0) was present in larger amounts, followed by myristic acid (C14:0). The free and bound lipid compositions of navane and varagu were different. Oleic (C18:1) and linoleic (C18:2) acids were in significant amounts in their free lipid fractions, whereas palmitic and lauric acids were present in the bound lipid fractions. In addition, the bound lipid fraction of varagu starch contained two unidentified fatty acids (~25%). The biological significance of the gross variations in qualitative and quantitative profiles of starch lipids is not understood. It is reported, however, that the starch lipids may act as templates for the amylose helix, that the phospholipid protects amylose chains during biosynthesis, and that branching (to form amylopectin) occurs only in chains that are not complexed (Baisted 1983).

Starch has been isolated (58% yield) from the seeds of rajgeera (*Amaranthus paniculatus* Linn.) (Panchal and Dave 1984). The small-sized (1–1·5 μ) starch granules had low amylose content indicating it to be of waxy-type. The starch had a GT range of 62–65°C.

The hydration characteristics of starches, flour and semolina from different cereal grains have been studied (Chandrashekar and Desikachar 1984). Sorghum starch absorbed much more water at 80°C than wheat and maize starches, probably due to the differences in the qualitative/quantitative makeup (chain length, M_r, etc.) of starch *per se*. On the contrary, sorghum semolina absorbed less water, and this was essentially due to starch-protein interactions, as treatments with either a protein solvent (tertiary butanol) or papain increased water absorption (chandrashekar 1985).

The starch as well as free sugar and protein contents of different varieties (sweet and non-sweet) of sorghum were negatively correlated with tannin and mineral matter contents of the seed (Arora and Luthra 1972). This is in agreement with the fact that genotypes differ very considerably in their ability to absorb nutrients and consequently in their adoptation to varying soil environment.

Varietal differences were studied in the isolated starches of 16 sorghum samples (Chandrashekar 1985). The content of amylose varied from 24–36%, of which the water-soluble amylose ranged from 9–22%. There were differences in the water uptake of the starches but only small differences in the paste viscosity. The intrinsic viscosity of the starches varied from 0·6–1·0. Also considerable variations in the rate of amylolysis with pancreatic α-amylase were noticeable. Besides, differences were noticed in the properties of starches (Chandrashekar 1985) from different parts of the grain.

A much more accurate estimation of amylose is reported by the use of a double-wavelength method of determination of the iodine-complex.

4.2b *Processing and technological studies*: A considerable amount of work has been carried out on rice (*Oryza sativa*) concerning its chemical, functional and technological aspects. Numerous varieties of rice have been analysed for their milling, cooking and product-making attributes. Specifically, it is observed that the qualitative/quantitative nature of the starch that determine the end-use of different varieties of rice vary from one variety to another. It is found that the amylose content, its water solubility and the GT of the respective starch play a significant role in the quality of rice varieties (Indudharaswamy and Bhattacharya 1982a). In one extreme, waxy varieties contain no amylose (or very little amylose) and become extremely soft and sticky after cooking. At the other extreme are high amylose (which also includes high water-insoluble amylose) varieties which become hard and flaky after cooking. The product making quality such as puffing of rice are also dependent on the rice starch properties (Murgesan and Bhattacharya 1986). For brewing purpose low gelatinization varieties, and for making certain baby foods intermediate-amylose varieties are preferred.

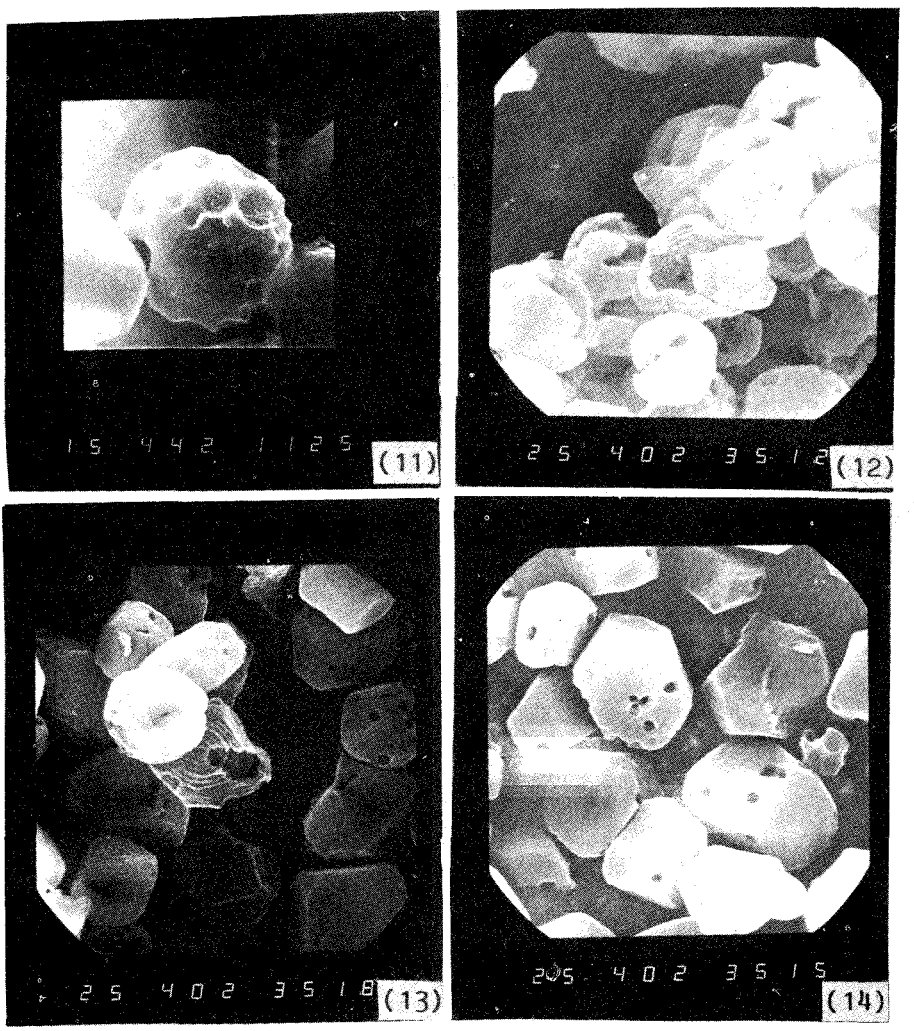
Processes such as parboiling, flaking and puffing of rice varieties have been found to be governed by the starch characteristics (Bhattacharya 1985). Parboiling involves primarily starch gelatinization followed by its retrogradation (Bhattacharya and Ali 1985). In the process of making rice flakes, starch retrogradation is largely prevented, but the starch granules are subjected to mechanical damage resulting in the rapid hydration of flaked rice (Ali and Bhattacharya 1976). On the other hand, during puffing the starch granules are irreversibly damaged and gelatinized. As a result of these changes the rheological behaviour of the final products are also altered, some of which may have the desired industrial applications (Chinnaswamy *et al* 1984).

The content of damaged starch in wheat flour of Indian varieties have been determined by 4 different methods (Tara and Bains 1972). These essentially consisted of susceptibility of damaged starch granules to hydrolysis by amylases. As a result of this, the wheat flours gave high maltose value, which is necessary for bread making. It is an indication of the ability of a flour for gas production by the action of yeast in the dough, and for bringing about desirable changes by the action of α-amylase on starch during baking. Further, the presence of damaged starch in wheat flour also contributes to its high water absorption.

4.2c *In vitro digestibility studies*: A good deal of research has gone into the study of the kinetics of amylolysis of native millet starch granules followed by SEM observations of the enzyme-digested granules (R N Tharanathan, unpublished results). In all these the enzymatic attack was by exocorrosion, i.e. attack from the exterior portion of the granule (or molecule!) inward. Further, the amylolysis proceeded most rapidly in the 'amorphous' or the less crystalline regions of the molecule. The rate and extent of amylolysis was essentially a cumulative action by several factors such as (i) the presence of contaminating enzymes in the amylases; (ii) the stability of the enzyme preparation over a period of time; (iii) the enzyme to substrate ratio; (iv) its 'debranching' ability to hydrolyse large and small substrates; (v) the availability of non-reducing ends at its surface; (vi) the overall composition of the starch *per se*, particularly the amylose content and its chain length (DP); and (vii) shape-size variations in the granule population as also on the interactions between granules of different sizes. Small spherical granules were reported to be less digestible than the big hexagonal granules. Higher the content of amylose, slower is amylolysis (Ueda *et al* 1974).

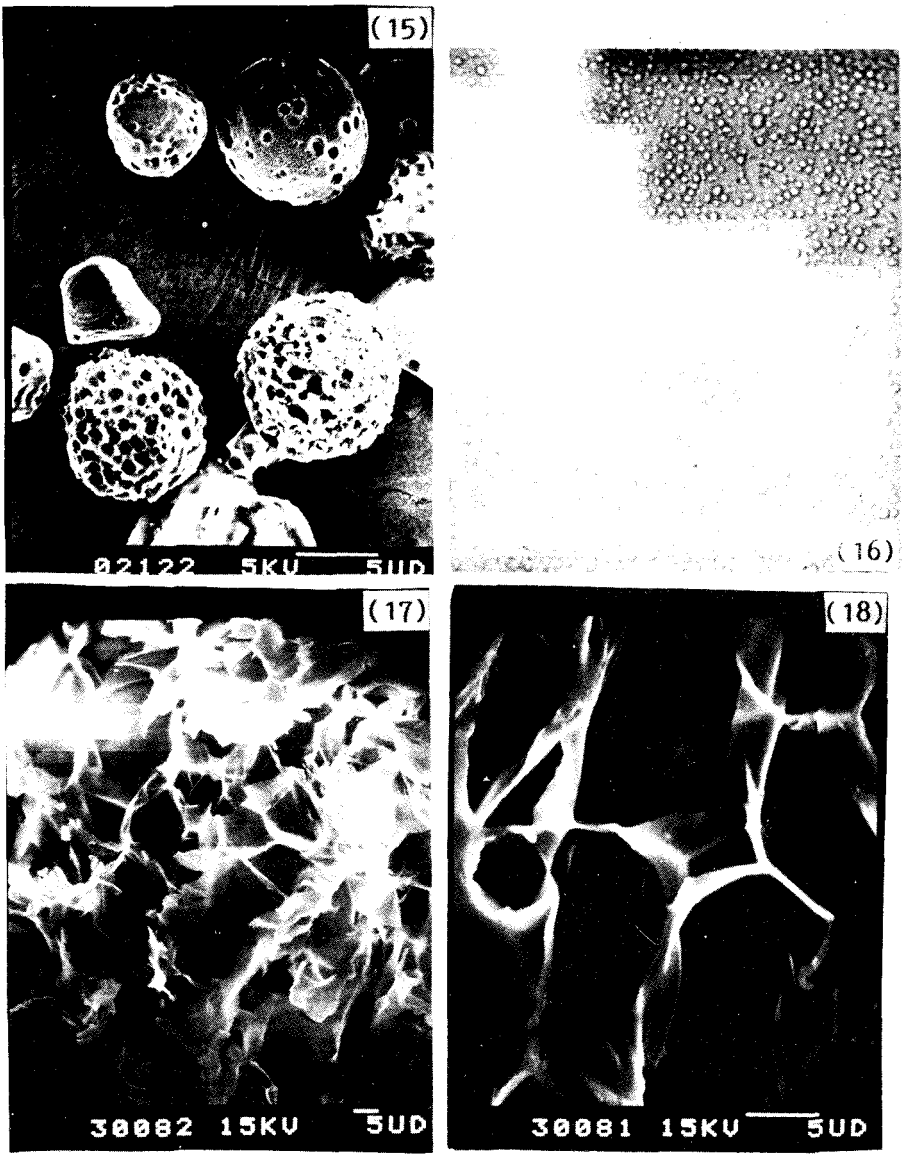
In SEM, some of the native granules showed surface indentations (scars, figure 10) probably as a result of compression of the small granules (or protein bodies) against the larger granules during the later stages of development in the amyloplast (Paramahans and Tharanathan 1980). Morphological characteristics of 'pitting' and internal layering was invisible in ragi (Tharanathan *et al* 1980) and varagu (Paramahans and Tharanathan 1980) starches, although the release of reducing sugars indicated rather extensive amylolysis. However, varagu starch did show innumerable hollow depressions all round the surface and also the granules appeared porous (figure 11) (Paramahans and Tharanathan 1980). The attack by glucoamylase was far more uniform and resulted in pitting and depressions all over the granular surface.

The starches from 'navane' (Ramadas Bhat *et al* 1983), samai, sanwa (Tharanathan



Figures 11–14. **11.** SEM of varagu starch granules attacked by glucoamylase, indicates the porous nature of the granule. **12.** SEM of navane starch granules attacked by salivary α-amylase. **13.** SEM of panivaragu starch granules attacked by salivary α-amylase, indicates internal layering. **14.** SEM of panivaragu starch granules attacked by glucoamylase.

et al 1983) and panivaragu (Ramadas Bhat *et al* 1983) were more susceptible to the action of glucoamylase and α-amylase. The granules were attacked by these enzymes almost to comparable extents. In contrast to the native granules where distinct hexagonal and polygonal shapes were visible, majority of the attacked granules had lost their characteristic shapes and had become spherical (figure 12). This indicated a preferential enzyme attack at the hexa- or polygonal sites. Layered internal structures were observable in some granules (figures 13–15). In the 'tunnelling'-type of attack



Figures 15–18. **15.** SEM of sanwa starch granules attacked by glucoamylase, indicates layering and pepper potting. **16.** Photomicrograph of pepper starch granules under ordinary light. **17.** SEM of popped ragi starch granules, indicates flaky nature of the granules. **18.** SEM of popped bajra starch granules.

some degree of difference could be noted between glucoamylase and α-amylase. According to Evers *et al* (1971) in the case of attack by glucoamylase, the 'disc-like' depressions taper in such a way that the diameter of the pit progressively diminishes inwards. α-Amylase, on the other hand attacks the surface forming pits which get broadened in the interior of the granule than at its surface. However, in some cases in the same granule population a range of enzyme degradation patterns such as single or multiple large hole tunnelling, pitting all over the granular region, selective surface erosion resulting in layered internal structures, 'pepper potting' causing innumerable small punctures with subsequent cracks and opening up of granule and some granules resisting any attack were also seen. There is no coherent explanation for the variety of effects seen.

4.3 *Tuber starches*

4.3a *Physico-chemical studies*: Next to corn starch, tapioca starch is used most extensively in India. Its starch is obtained from the roots of the tapioca plant (*Manihot utilissima*). Some processing studies on tapioca starch have shown that the content of amylose and the extent of its solubility in water play a role on the eating quality of tapioca (Pai 1984). Changes similar to those in rice occur during the preparation of parboiled tapioca. However, on prolonged cooking, tapioca starch is highly unstable, i.e. the initial high viscosity falls rapidly with cooking and finally results in a watery paste (Srivastava and Patel 1973). Such a property is not useful for the use of tapioca starch for sizing of cotton in textile industries. Accordingly, studies were initiated to modify the starch by way of crosslinking to alter the viscosity properties.

From elephant yam (*Amorphophallus campanulatus*) starch was isolated in 12·5% yield (Wankhede and Umadevi 1981). After peeling off the outer coat, the root tuber was cut into small pieces and then homogenized in a waring blender for quantitative starch recovery. The granules were mostly polygonal, and containted ~25% amylose (table 5). As compared to native granules the gelatinized starch was hydrolysed better by amylases.

Dioscorea ballophylla is a climber tuber consumed mostly by the tribal people. *A. campanulatus* is a stout herbaceous plant with an underground corn, which is used for curries and pickles only after long washing and prolonged cooking. Starches have been isolated from them (35% yield). which contained ~2·5% protein and

Table 5. Granule characteristics of miscellaneous starches.

Source	Shape	Size (μm)	Protein (%)	Amylose (%)	Amylo-pectin (%)	GT range (°C)	References
Banana pseudostem	Irregular	15–20	—	21	79	NA	Subrahmanyan *et al* (1957)
Yam elephant	Polygonal	7–30	0·3	25	75	73–81	Wankhede and Umadevi (1981)
Sangara	Irregular	5–19	0·1	NA	NA	72–78	Panchal and Dave (1984)
Makhna	Round-polygonal	5–20	—	21	79	ND	Nath and Chakraborty (1985)
Coleus	Round	5–20	—	33	67	65–85	Abraham and Mathew (1985)
Dioscorea	Elliptical	5–20	2·5	18–24	75	75–80	Soni *et al* (1985)
Black pepper	Round-polygonal	2–2·5	1·4	18	82	70–75	Ramadas Bhat and Tharanathan (1983)

NA, Not available.

amylose (18–24%) (Soni *et al* 1985). The granules are elliptically shaped and are interspersed with a protein matrix. The granules have a high degree of association, and a high GT range (75–80°C). They had two stage swelling behaviour indicating that there are two types of forces requiring different energy inputs to cause relaxation. In comparison to tapioca starch, the amylograph data showed high peak viscosities for *A. campanulatus*, and low peak viscosity for *D. ballophylla*.

Cassava (*Manihot esculenta* Crantz) is a tuberous root indigenous to tropical countries like India. Dry cassava flour contains ~85% starch (Abraham *et al* 1979).

As novel sources of starch, tubers such as kante kangi (*Dinebra arabica*), kurka (*Coleus pariflorus*), yam (*Dioscorea alata* and *Dioscorea bulbifera*) have been studied (Modi 1982). Phosphorus as α-D-glucose-6-phosphate was invariably present in tuber starches, in contrast to cereal starches where phosphorus is present as phospholipid which is easily extractable with organic solvents.

A yield of 14% starch was obtained from *Coleus parviflorus*. The granules were round shaped (5–20 μ) and contained 33% total amylose of which soluble amylose represented 12·8% (Abraham and Mathew 1985). Its GT range was 65–85°C, and showed two stage swelling. It was easily soluble in DMSO and exhibited A-pattern on x-ray diffraction. The starch was somewhat resistant to amylase action (Moorthy 1986). Relatively small starch granules (3–15 μm) have been isolated from an Indian crocus (*Crocus sativus*) (Craig *et al* 1985). The granules appear to have a very close packing, as shown by their rough surface and flattened facets. The starch had an amylose content of 27%. Gel permeation chromatography on Sepharose-2B indicated a ratio of 72:28 for the excluded to included material.

4.4 *Starch from spices*

Black pepper (*Piper nigrum*) is an important spice of great commercial value. Unusually small sized (~2 μm) starch granules were isolated in 25–38% yield (figure 16) and partially characterized (Ramadas Bhat and Tharanathan 1983). The starch (table 5) had an amylose content of 18%. It was non-ionic and exhibited low solubility and low swelling power in water, but high solubility in DMSO. The Brabender amylogram peak viscosity of pepper starch was about 530 BU with a very little set back (550 BU) on cooling. This granule stability and resistance to retrogradation suggested that the black pepper starch has a high degree of association between the linear and branched (amylopectin) components that maintain the granular matrix. Such macromolecular association confers resistance to mechanical shear upon gelatinization, a property exhibited by modified (e.g. cross-linked) starches. X-ray diffraction pattern revealed the starch granules to be of the A-type.

4.5 *Starch from aquatic plant and miscellaneous sources*

Sangara is an edible aquatic plant grown widely in ponds and lakes. Starch has been isolated from the kernels by a process of maceration and centrifugation (Panchal and Dave 1984). The starch granules appear quite big (19 μm), having pronounced oyster shell-type striations. Interestingly, sangara starch displays on Brabender viscograph no drop in peak viscosity even on continued cooking, a behaviour characteristic of cross-bonded starches.

Euryale ferox (also called 'makhna') is an aquatic fruit often consumed by tribal people as a source of protein (7·3% protein in the seeds). The fruits contain 140–150 seeds per fruit. Starch has been isolated in 20% yield (Nath and Chakraborty 1985). It has 21·2% amylose. Structural analyses of the individual fractions have also been reported.

Fairly white starch has been isolated from sal (*Shorea robusta*) and dhupa (*Vateria indica*) seeds (R N Tharanathan, unpublished resuts). As the seeds were highly coloured, prior processing with chlorine water/hydrogen peroxide solution was desirable to get a white starch. The recovery of starch was 25–30% of the defatted material. X-ray diffraction pattern revealed both the starches to be of A-type. A few preliminary characteristics of these starches have also been studied.

4.5a *Modified starches and uses*: In order to meet the specific requirements of various food and non-food industries, starches have been modified by a variety of procedures.

Oxidised starch is one such derivative used in paper and textile industries (Srivastava 1974). The most commonly used oxidising agent is sodium hypochlorite at acidic, alkaline and neutral pHs. The oxidation is non-specific and brings about the conversion of hydroxyl groups into carbonyl and carboxyl groups, which results in profound changes in their physical properties, such as a decrease in GT as well as the viscosity, suppression of retrogradation and increase in solubility. In addition to oxidation, the reaction involves some degree of depolymerization which is prevented by the use of suitable catalysts.

Hydroxyethyl (or hydroxypropyl) starch is prepared by reacting starch with ethylene oxide or propylene oxide in alkaline medium (Srivastava 1974). Depending upon the degree of modification and distribution of the substituent groups in the main chain the properties of the derivatives change enormously, a decrease in GT, suppression of retrogradation and increase in paste clarity and its cohesiveness. Employing Smith degradation the distribution of 2-hydroxyalkyl groups could be determined. The results showed 84% substitution at 0–2 and the remaining 16% mainly at 0–6 (Srivastava and Ramalingam 1967). Hydrolysis with dilute sulphuric acid followed by chromatographic analysis is another useful method for locating the hydroxyalkyl groups (Srivastava *et al* 1969, 1970d).

Some studies have also been conducted on the modification of black gram starch by heat and moisture treatments, acetylation, oxidation, cross-linking and adding free fatty acids (Deshpande *et al* 1982). All the modified starches showed a lowering of GT by 1–6°C, but in the fatty acid modified starch GT raised by 1–4°C. Compared to raw starch, the solubility profile of the modified starches was affected, particularly the fatty acid-treated and cross-linked starches were less soluble. At pHs 2 and 10 all of them had greater swelling capacity and solubility.

Starch dextrins have a vast array of applications in food, non-food and pharmaceutical industries. The reaction involves heating starch in the dry state (10–12% moisture) at 190°C for 10–24 h, which results in dehydration and trans-glycosidation besides cleavage of the glycosidic bonds. Dextrinization of corn starch gave a product with an increase in solubility and decrease in β-amylolysis (Srivastava *et al* 1970c). A mechanism of dextrinization has been proposed (Srivastava 1974). It involved essentially a cleavage of molecular chains to smaller units which are terminated by anhydro sugar residues of the levoglucosan-type. Although there is a

tremendous decrease in the molecular size, the degree of branching is considerably increased. α-1,6-, β-1,6- and β-1,2-linkages are formed at the expense of α-1,4-linkages.

Acid dextrinization of corn and tapioca starches in 0·007% HCl and $MgCl_2$ for 8 h gave a series of products of differing physico-chemical characteristics (Srivastava 1974). The initial rapid breakdown of the polymer (1 h) was followed by trans-glycosidation.

Pyrodextrins have been prepared from ragi, wheat, jowar and rice starches (moisture content of 8%) by heating them at 200°C in the absence of any catalysts (Wankhede and Umadevi 1982). The resulting products had increased solubility, reducing power and alkali lability values. Considerable decrease in β-amylolysis limit and iodine affinity values were correlated with initial hydrolysis, and transglycosidation resulting in an increased degree of branching and elaboration of thermally degraded products.

Copolymerization of starch with other polysaccharides results in the fusion of the fragments of both the polysaccharides. Codextrinization of corn starch and gum karaya in 9:1 and 9:6 ratios at different temperatures and time intervals showed a catalytic effect of gum karaya on the dextrinization of starch (Srivastava 1974). This was attributed to the acetic acid liberated during the reaction (from the –OAc groups in native gum karaya). The purified codextrin upon hydrolysis yielded D-glucose, D-galactose, L-rhamnose and D-galacturonic acid. Definitive proof of polymer fusion ('grafting') was established by the isolation of a few hetero-oligosaccharides.

Similarly guar gum was codextrinized with corn starch in various proportions at 153°C for 8 h, in the presence of HCl (pH 3) (Srivastava 1974). Solubility studies revealed that the dextrinization of starch was considerably inhibited by guar gum, probably due to the presence of nitrogenous compounds, especially glycine in the guar gum (Srivastava 1974). Studies with model compounds were later on carried out to confirm this observation (Srivastava 1974). This inhibition is attributed to the acid-binding or buffering action of amino acids and proteins. Dextrinization also resulted in the generation of free amino groups due to degradation of proteins. In addition to the inhibitory effect, the free amino acids, peptides and proteins took part in the non-enzymatic browning reaction. The latter is of very great significance in food processing.

The various types of dextrins—canary dextrin, white dextrin and pyrodextrin (also called British gum) produced from starch are useful as adhesives for paper and paper products. A variety of gums and starches have been codextrinized and their properties and usefulness studied (Srivastava 1974). Adhesive strength of a number of codextrins have been evaluated (Srivastava 1974). Codextrin prepared from starch-gum karaya had high adhesive strength.

Tapioca starch granules on cross-linking with sodium trimetaphosphate, phosphorus oxychloride or epichlorohydrin gave products having highly stable paste viscosity (Srivastava and Patel 1973). Even a very low concentration (0·01%) of epichlorohydrin at pH 11 stabilized the paste viscosity. By changing the degree of cross-linking products of desired viscosity characteristics were obtained. However, extensive cross-linking resulted in ungelatinizable starches which are of use as surgical dusting powders and as carriers for electrolytes in dry battery cells (Srivastava 1974). The stabilization effect imparted by cross-linking is due to the fact that cross-bonding of the surface of starch granules results in tight macromolecular

net work such that after initial swelling in water the granule which increases several times its size is still strong enough to maintain its integrity without bursting and loosing the imbibed water. On excessive cross-linking the granule becomes too restricted for hydration and swelling.

4.5b *Starch in relation to cooking*: The cooking quality of legumes was partly found to be related to the nature and content of starch (Narasimhan 1984). Good cooking *dhals* from red gram (*Cajanus cajan*) had a slightly higher content of starch, whereas in the poor cooking *dhals* the content of insoluble amylose was more.

Variations were also observed in the swelling property of cells and starch granules during cooking of different varieties of red gram, the poorer cooking *dhals* showed lesser expansion rate, both of starch granules and cells (Narasimhan 1984). There was also a greater tendency for clustering of cells and starch granules.

A weaning food formulation has been developed out of malted finger millet and malted mung bean (Malleshi and Desikachar 1982). The malt enzymes present in the germinated grains hydrolyse starch during the heating of the slurry, thus resulting in low paste viscosity but increased caloric density. The formulation was well accepted by children. It also showed good growth promoting response.

4.5c *Germination and malting studies*: A few reports are available on the effect of germination on carbohydrate status of plant materials. As starch is the reserve carbohydrate of a vast majority of plants extended period of germination (over 24 h) results in elaboration of different carbohydrases particularly amylases/phosphorylases followed by gradual degradation of starch molecules (Malleshi 1984; Venkatanarayana 1984). As a consequence, the content of free reducing sugars as well as amylase increases. Starch isolated from germinated chick pea and green gram exhibited better swelling power and solubility but lower intrinsic viscosity (Jaya and Venkataraman 1980). A similar result was obtained for horse gram and moth bean starches (Subbulakshmi *et al* 1976). The nutritional value of these legumes increased after germination, as they were better digestible. It was reported that during germination there was a selective degradation by amylase and phosphorylase of amylopectin with a concommittant increase in the amylose content (Ganeshkumar and Venkataraman 1976). Because of these changes the overall physical properties of starches were also altered. As a result, a favourable impact on the digestibility, the flatus-forming property and other nutritional qualities of the legumes were also observed (Ganeshkumar and Venkataraman 1976).

SEM of starch granules from germinated horse gram showed pronounced pitting with occasional hollow depressions all around the surface (El Faki *et al* 1983b). SEM of starch granules of germinated chick pea showed hardly any morphological aberrations: this indicates that the enzyme action is sluggish during germination (El Faki *et al* 1983b). This is probably an indication of low enzyme activity and/or low susceptibility during this period of germination. Comparatively horse gram germinated better and at a faster rate than chick pea and cowpea (El Faki *et al* 1983b). Accordingly SEM revealed pronounced pitting with occasional hollow depressions all around the area. SEM of germinated cowpea starch granules showed discrete surface layering (El Faki *et al* 1983b).

Studies have been made on the fate of red gram starch (6 varieties) during

progressive germination (Sharma and Pant 1979; Jaya and Venkataraman 1980). The various enzymes involved in the scission of starch molecule were partially characterized. Two distinct phases of starch depletion were recognized. It was found that during germination starch is mainly subjected first to slow degradation by phosphorylase followed by rapid degradation with maximal activity of α-amylase. Electrophoretic studies revealed only one molecular form of these two enzymes.

Comparative studies have been made on the malting characteristics and nutritive value of malted flours of some tropical cereals and millets (Malleshi and Desikachar 1986b). Ragi malt is one of the popular products prepared from sprouted ragi, and it finds applications in the preparation of weaning foods, beverages and nutritious foods. Several new varieties have been tested for their malting quality (Malleshi and Desikachar 1979, 1986a). Varieties with poor germinating power and low amylase activity were not well suited for malting. Pearl and finger (ragi) millet malts exhibited high α-amylase activity within 2–3 days of germination; whereas maize, sorghum, wheat and triticale malts showed high enzymic activity only after 4–5 days of germination (Malleshi *et al* 1986b). After malting, the paste viscosity of the flour was significantly lowered, amylase activity increased, and the malts exhibited desirable flavour and taste. However, pearl millet malt was bitter and developed rancidity within a week after preparation (Malleshi *et al* 1986b). Continued germination (upto 96 h) resulted in 10% loss of starch and slight lowering of protein content. The suitability of sorghum and finger millet for malting and subsequent use in weaning food formulations have also been tested (N G Malleshi, unpublished results). In addition, malting has several other nutritional benefits, such as increase in the contents of vitamins, lysine and tryptophan.

A few physico-chemical properties of native and malted millet starches have also been studied (Malleshi *et al* 1986). In comparison with native starches, malt starches contained a majority of smaller granules, slightly more amylose and exhibited higher GT, lower swelling power, higher solubility in water and DMSO, and lower intrinsic viscosity. The *in vitro* digestibility of the malted starches was more or less similar.

A number of studies were reported on changes in carbohydrates in developing seeds of various legumes. In red gram there was a rapid accumulation of starch between 14 and 28 days after flowering but an increase in free sugar content upto 35 days followed by their decline (Singh *et al* 1981). The former effect was accompanied by a decline in the pod wall, indicating that seed and pod wall did not compete with each other for starch accumulation.

4.5d *Popping and puffing studies*: Some studies have been made on the effect of popping quality *vis-a-vis* the starches of cereal grains. Popping of cereals is a well-known traditional method of processing. It is a simple and least expensive method of preparing ready-to-consume cereal products. During popping the kernel is subjected to high temperature for a short time, and this brings about spectacular changes in the starch characteristics. Among the 20 strains of sorghum studied large varietal differences were found in popping quality (Chandrashekar 1985). The hardness of the unpolished grains as well as the size and density of polished grain were related to the volume expansion, mostly of the corneous endosperm, during popping. The set back viscosity of sorghum flour of good popping quality was higher than those of poor popping quality. The starch characteristics of these varieties were also different (Chandrashekar 1985).

Starches were also isolated from popped bajra, ragi and 'navane' (Muralikrishna *et al* 1986). Popping resulted in a complete loss of birefringence (due to gelatinization) characteristics of starch granules, an increased solubility in DMSO, a low cold-paste and set-back viscosity and a lower relative viscosity in KOH. Although the granules expanded enormously they retained hexa-/polygonal nature. A few granules had lost their granular matrix and appeared flaky (see figures 17 and 18). Popped starches in comparison to native starches exhibited higher susceptibility to *in vitro* enzymatic digestibility. However, popped 'navane' was less digestible because of its low degree of gelatinization. This probably was due to the presence of hard seed coat on navane grain, which may prevent effective heat transfer (Muralikrishna *et al* 1986).

Preliminary studies indicated that chick pea has better puffing quality than cowpea and horse gram (El Faki *et al* 1983b). From puffed chick pea and horse gram (poor puffing) starches were isolated and compared (El Faki *et al* 1983b). The starch granules of the former showed restricted swelling and typical doughnut or 'swimming ballon' -like structure (figure 19A) in SEM. The average size of the puffed granules was more than the unpuffed ones. A deeper depression is shown by the completely expanded granules, while those which are slightly or half puffed do not show this property. Apparently, the small spherical granules were not affected except for their volume increase due to swelling. Horse gram starch granules do not show this property. Most of these granules are completely gelatinized forming lumps of irregular shapes (figure 19B) with profound swelling. Such an observation has also been made in the popping of cereals. These differences in puffing quality are ascribed to the combined structural and compositional properties of starches *per se*.

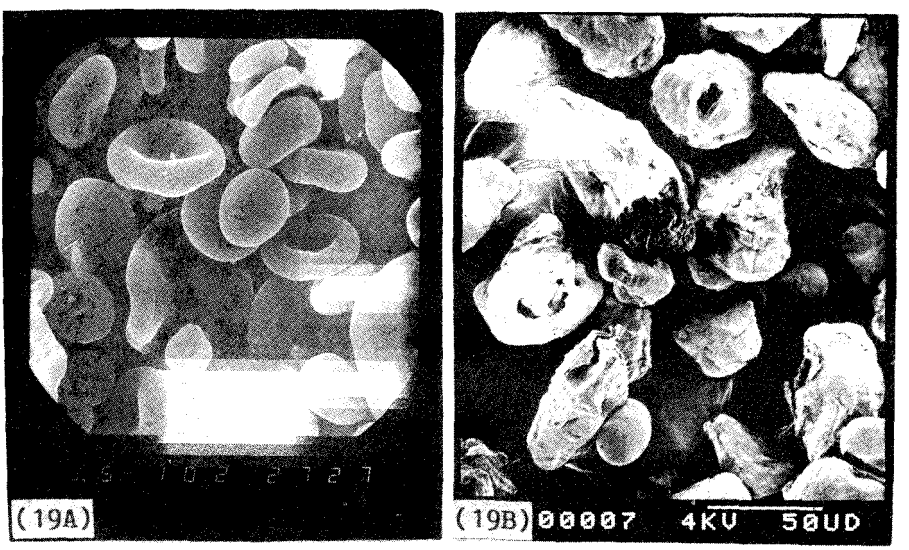


Figure 19. **a.** SEM of puffed chick pea starch granules, indicates doughnut or swimming ballon-like structure. **b.** SEM of puffed horse gram starch granules, indicates profound swelling and partial gelatinization.

5. Pectins

5.1 *Chemistry*

Pectin is regarded as a generic name and covers a wide range of polygalacturonates differing in their DP and of esterification (DE) and the nature of covalently bound sugars. Pectins derived from different sources vary widely in their gel forming properties because of the differences in length of their polygalacturonic acid chains and degree of esterification with methanol. Their composition also varies according to the method of extraction employed (Kertesz 1951). Pectin is a reversible hydrophilic colloid. Probably there are no two pectin preparations identical in their chemical structure.

Pectic acid (α-1,4-linked polygalacturonan), the parent molecule of the pectic group of polysaccharides, is not very common in plant tissues. More usually the chain is modified by methyl esterification of some (pectinic acid) or most (pectin) of the C-6 carboxyl groups. There is an infrequent insertion of rhamnopyranose units (α-1,2-linked), or substitution of side chains with D-galactose (α-1,4-linked) or longer side chains of L-arabinofuranose units which themselves are highly branched or by O-acetylation at 0–2/0–3 of a few of the units. The content of –OAc groups in pectins tend to reduce gel formation presumably by preventing hydrogen bonding, and the effects of esterification are to be found on a variety of properties related to gelling (Kertesz 1951).

Structural analyses have been carried out on field bean hull pectins (Salimath and Tharanathan 1982b). Three pectinic acids PA-1, PA-2 and PA-3 were isolated by extractions with ammonium oxalate and EDTA. These fractions varied in their viscosity behaviour, M_r, degree of esterification, extent of heterogeneity and neutral sugar profile. Further fractionation of PA-2 gave P_1-4. Both PA-1 and P_1-4 were homogeneous and consisted of 1,4-linked α-D-galacturonan core punctuated with occasional blocks of 2-0-linked L-rhamnopyranose residues. In addition, the backbone had single or multiple residue side stubs of L-arabinofuranose and D-xylose. Interestingly in field bean hulls a high content (6%) of pectins was found. The physiological function of these pectins in the hulls is not known.

Pectic substances were also detected in rice leaves (Mukherjee and Ghosh 1973). Its content decreased upto 12 days following inoculation with *Helminthosporum oryzae*, after which no significant change was noticed. The decrease in pectin content was mainly due to an increased activity of pectin degrading enzymes.

Sunflower (*Helianthus annus*) is a plant with oil-bearing seed. Pectin has been extracted from the seed with oxalic acid and ammonium oxalate (0·5% each) at 90°C for 30 min (Pruthi *et al* 1960b). Its content was found to increase from the stage of full blossom to the mature dried flower heads, but the jelly grade quality of the pectin simultaneously decreased. To a certain extent maturity resulted in demethylation of pectin (Pathak and Shukla 1981).

The use of chemical reagents for pectin extraction facilitates greater yield due to their calcium complexing property and as a result conversion of insoluble calcium pectate and protopectin into soluble sodium pectate and pectinic acid. A variety of chemical reagents have been used for quantitative extraction of pectin from guava (*Psidium guajava* L.) fruits (Dhingra and Gupta 1984). Ammonium oxalate-oxalic acid was the best solvent as it gave improved yield of crude pectin. Low concen-

trations (0·25%) gave high grade pectin having a higher jelly strength, whereas at high concentrations the quality of the pectin was seriously affected in that its equivalent weight, the methoxyl and galacturonic acid contents, and DE were altered.

From guava fruit pectin has been extracted with various solvents of which citric acid extraction gave maximum yield of good quality pectin (Pruthi *et al* 1960a). Fully developed green guava gave higher yield of good quality pectin than did yellow or over ripe fruits. Peel, flesh and core of guava contained 1·7, 0·6 and 0·5%, respectively of pectin. Enzymic hydrolysis of the pectin gave D-galacturonic acid, D-galactose and L-arabinose in 72, 12 and 4·4% yield, whereas acid hydrolysis resulted in 62, 8 and 6% yields, respectively.

Hot ammonium oxalate and citric acid extraction of the stem of *Agave vera cruz* Mill gave a pectin of poor quality with poor jelling character (Satyanarayana and Bhatia 1955). It consisted of D-galacturonic acid, D-galactose and L-arabinose.

The contents of pectin and polygalacturonase activity in two cultivars (Royal and Golden delicious) of apple were determined at pre-ripening, ripening and post-ripening stages (Kumar *et al* 1985). Pectin content was higher in the former. In the post-ripening stage a decreased pectin content was observed.

5.2 *Functional implications*

Pectic polysaccharides normally interact through non-covalent as well as through covalent bonding. The former type of interactions are predominant in interconnections between pectic and other cell wall polymers. Calcium is especially known to confer rigidity, through binding to free carboxyl groups of pectin to cell walls (Grant *et al* 1973). Pectic substances are mainly found in fruits and vegetables and in trace amounts in cereals.

Some studies are available on the functional behaviour of pectins in relation to cooking quality of legume *dhals* (Narasimhan 1984). The pectin content was less in good cooking *dhals* of red gram than in others. Free pectin rather than the total pectin content has a correlation to the cooking pattern. Here pectins not only reacted with calcium and magnesium present in the legume and reduced the cooking, but also restricted the swelling of starch granules. Their effect was more pronounced in the poor cooking *dhals*.

5.3 *Uses*

The total esterified groups (methoxyl) in a pectin preparation is 16·3% (Kertesz 1951). Low methoxyl pectins (LMP, methoxyl content in the range 2·5–4·5%) are very useful in the food industry (Kertesz 1951). For a stable gel formation the low methoxyl pectin should have free, at least 50% of the total (free + esterified) carboxyl groups. and these free carboxyl groups react with calcium to precipitate 75–90% of the total LMP (Padival *et al* 1979a). The material thus obtained holds 50–60 g of water per g and forms a stable gel. The solution changes that take place after the addition of calcium are classified into sol, soft gel, good gel, brittle gel and coagulated gel. Higher concentrations of Ca^{2+} results in incipient precipitation of LMP and loss of gel state. From lime peel LMPs have been obtained by acid and alkali treatments at different pHs (Padival *et al* 1979b). These preparations differed in

gelling characteristics; and had ~45% methoxyl groups and a M_r range from 40,000–70,000.

6. Gums and mucilages

6.1 *Gums*

A large number of gums (and mucilages) are available in India because of a wide variety of flora and fauna. Although a clear-cut demarcation between gums and mucilages is not easily possible, generally speaking gums are soluble in water, whereas mucilages are insoluble in aqueous medium (Tharanathan 1977). Gums have irregularly spaced side chains along the otherwise linear structures, and mucilages have regularly spaced side chains (Smith and Montogomery 1959).

Plant gums are of exudate or seed origin. Exudate gums are spontaneously formed as viscous fluids at the site of injury to the plant and which become dehydrated to give hard, clear nodules. In a way exudate gums play a defensive role to protect the plant from infection at the place of injury to the tissue, and further to prevent loss of moisture. On the other hand, seed gums (as well as mucilages) probably function as reservoirs for the retention of water, and thus help protecting the seeds (or different tissues of the plant where they are found) from dehydration. The latter phenomenon might induce protein denaturation, especially of enzymes necessary at the onset of seed germination.

6.1a *Chemistry and structure*: Exudate gums are the earliest known gums from the indigenous trees and bushes belonging to various geographical areas. Many plant gums are known but only a few are of commercial importance, and are well characterized. Gum arabic (*Acacia* trees), gum karaya (*Sterculia urens* tree), gum tragacanth (exudate from *Astragalus* species), gum ghatti (exudate from *Anogeissus latifolia*) are some of the gums studied in detail. Probably the gum secretion is a part of normal physiological phenomenon. Structurally all of them are complex acidic polysaccharides.

Bael (*Aegle marmelos*) plant is abundant in India. The fruit pulp and the gum are known for antihistamic action and are also used against dysentry and diarrhea. The purified gum from bael tree contains D-galactose, L-rhamnose, L-arabinose and D-glucuronic acid (9 : 3 : 1 : 3) (Roy *et al* 1975, 1976, 1977; Mandal and Mukherjee 1980). Autohydrolysis of an aqueous solution of the gum yielded a degraded gum. Structural investigations in detail performed on the native, degraded and carboxyl-reduced whole gum revealed a backbone of 1,3-linked β-D-galactopyranose attached with side chain stubs in different linkages. From bael seeds a gummy material was recovered which possessed a similar backbone structure but varying in the nature and mode of attachment of side chain units (Mandal and Mukherjee 1981).

The exudate gum from *Spondias dulcis* (*Anacardiaceae*) is used as a refrigerant. On acid hydrolysis the purified gum gave galactose (19·8%), arabinose (48·5%) and galacturonic acid (20%) (Basu and Rao 1981). On autohydrolysis it gave a degraded gum composed of D-galactose, L-arabinose and D-galacturonic acid (3 : 3 : 1). The whole gum possessed a 1,3-D-galactan core substituted with arabinopyranose,

arabinofuranose, galactose and galacturonic acid residues in different linkages; whereas the degraded gum had a similar core devoid of some of these side chain stubs (Basu and Rao 1981).

From the gum exudate of *Spondias pinnata* a homogeneous acidic polysaccharide has been isolated and structurally characterized (Ghosal and Thakur 1981). Its degraded product obtained by autohydrolysis contained D-galactose, L-arabinose and D-galacturonic acid. Methylation analysis revealed the probability of a 1,3-linked galactan backbone possessing unbranched interior branch chains composed of 1,4-linked galactose and 1,2-linked arabinose. D-Galacturonic acid was involved both as non-reducing terminus and as 1,4-linked units.

The purified polysaccharide isolated from jeol gum (*Odina wodier* Roxb.), an exudate, contained L-arabinose and D-galactose (1 : 2) together with 14·5% uronic anhydride (Bhattacharya and Rao 1964). Mild hydrolysis with 0·1 N H_2SO_4 gave an aldobiouronic acid characterized as 3-0-(D-galactopyranosyl uronic acid)-D-galactopyranose. Due to the high complexity in the molecular architecture of the whole gum, structural studies were carried out only on the autohydrolysed gum. Sequencing studies together with methylation/oxidation experiments showed the degraded gum to be a 1,6-linked D-galactan having single residue side chains of D-galacturonic acid at 0–3 and D-galactose at 0–4 and/or 0–3. The glycosidic linkages were mostly β.

The gum exudate collected from the drumstick plant (*Moringa oleifera*) is well known in India because of its medicinal values. The purified whole gum was found to be composed of L-arabinose, D-galactose, D-glucuronic acid, L-rhamnose, D-mannose and D-xylose in 14·5 : 11·3 : 3 : 2 : 1 : 1 ratio, respectively (Ingle and Bhide 1954a; Bhattacharya *et al* 1982). On mild acid hydrolysis (15 mM TFA at 100°C for 6 h) a degraded polysaccharide consisting of D-galactose, D-glucuronic acid and D-mannose (11·7 : 1:3·9) was isolated. Structurally this was found to be a 1,6-D-galactan having innumerable side chains at 0–4.

Sweetenia mahogany (belonging to *Meliaceae*), a medicinally and economically important plant, exudes a gum at the injured sites. The purified polysaccharide was composed of D-galactose, L-arabinose, L-rhamnose and D-galacturonic acid (37 : 5 : 4 : 10) (Ghosal and Thakur 1983). The degraded polysaccharide obtained on mild acid hydrolysis contained these sugars in 37 : 3 : 1 : 10 ratio, respectively. Its structural analysis was compatible with a highly branched backbone of 1,3-linked D-galactan chain. End-group analysis showed the polysaccharide to be of high DP (Ghosal and Thakur 1983).

The mangle gum from a useful medicinal plant (*Rhizophore mangle* Linn.) gave rise on autohydrolysis, a polysaccharide which consisted of L-arabinose, D-galactose, L-rhamnose, D-galacturonic acid and 4-0-methyl-D-glucuronic acid (15 : 13·5 : 26·7 : 36 : 4·1) (Sarkar and Rao 1975). Its primary structure was established to be 1,2-/ 1,4-linked L-rhamno-D-galacturonan having side chains at 0–3 of galacturonic acid, of galactopyranose terminated by L-arabinofuranose and 4-0-methyl glucuronic acid. The whole gum showed cross-reactions with *Pneumoccocus* antisera of different types, which gave a clue to various structural features of the intact polysaccharide. From graded hydrolysis 5 neutral and 4 acidic oligosaccharides were isolated and structurally characterized.

The gum from *Acacia catechu* is composed of D-galactose, L-arabinose, D-

mannose and D-glucuronic acid (9:4:3:3) (Hulyalkar *et al* 1956). On acid hydrolysis the gum yielded an aldobiouronic acid identified as 6-β-D-glucuronosido-D-galactose.

The gum from the plant *Lannea grandis* Dennst. is a polyuronide composed of galactose, arabinose and 4-0-methyl-glucuronic acid in 5:1:1 mol ratio (Parikh *et al* 1956). A few light-scattering studies are reported (Chaudhuri and Mukherjee 1967). The gum has a 1,6-D-galactan backbone having side chains of arabinose, galactose and galacturonic acid residues in different linkages.

The gum from *Moringa pterygosperm* Gaertn. consisted of arabinose, galactose and glucuronic acid (10:7:2) (Kurup and Narasimha Rao 1954). A trace of rhamnose was also present.

The gum from *Feronia elephantum* Correa plant consists of arabinose, galactose, xylose and traces of rhamnose and glucuronic acid (Mathur and Mukherjee 1954). The aldobiouronic acid was identified to be 3-0-(D-glucopyranosyl uronic acid)-D-galactopyranose. The gum had essentially 1,3-linkages.

The gum from *Schrebera swietenooides* Roxb. on acid hydrolysis gave galactose, fructose and mannitol (70%) (Ingle and Bhide 1954b).

An acidic gum was isolated from *Salmalia malabarica*, which consisted of L-arabinose, D-galactose, D-galacturonic acid and traces of L-rhamnose (Bose and Dutta 1963). By partial hydrolysis, an aldobiouronic acid, 6-0-(β-D-galactopyranosyl uronic acid)-D-galactose was identified. Periodate oxidation data also supported high branching in the molecule.

Complete hydrolysis of *Chloroxylon swietenia* gum revealed D-galactose, L-arabinose, D-galacturonic acid and 4-0-methyl-D-glucuronic acid (Bose *et al* 1963). Graded hydrolysis gave 6-0-(α-D-galactopyranosyl uronic acid)-D-galactose and a degraded gum composed of the same sugars in different proportions (Bose *et al* 1964). Structural investigations revealed a highly branched structure of 1,6- and 1,3-linked D-galactose in the main chain and side chain residues of 1,5-linked arabinose and 1,3-linked D-galacturonic acid (Bose *et al* 1968).

Structural studies on hualtaco gum from *Laxopterygium huansango* revealed a backbone of 1,3-linked D-galactopyranose residues having branches at 0–6 of some of the residues (Rao and Samajpati 1972). In some places branches consisted of single units of D-galactose and L-rhamnose and in some others aldobiouronic acid residues were present. Some of the acidic sugars are linked at 0–4 either to an L-arabinofuranose or to β-D-Gal-1,3-L-Ara residue (Rao and Samajpati 1972).

Eucalyptus gum contained D-xylose and 4-0-methyl-glucuronic acid. From the results of methylation, optical rotatory dispersion and kinetics of periodate oxidation the polysaccharide was found to be a 1.4-β-D-glycan containing one 4-0-methyl-glucuronic acid residue attached by a 1,2-linkage on an average to every tenth D-xylopyranosyl residue (Singh *et al* 1973).

A series of investigations have been made on the gum obtained from *Albizzia procere* Beuth. The purified gum was composed of D-galactose, L-arabinose, L-rhamnose (6:4:1), traces of D-mannose and glucuronic acid and its 4-0-methyl derivative (Farooqi and Kaul 1963). The gum showed properties similar to those of gum arabic. On autohydrolysis L-rhamnose, L-arabinose, traces of D-galactose and 3-0-D-galactopyranosyl-L-arabinofuranose were identified (Farooqi and Kaul 1965b). On mild acid hydrolysis two disaccharides, viz 4-0-(4-0-methylglucuronic acid)-D-galactose and 2-0-(D-glucuronic acid)-D-mannose were detected (Farooqi

and Kaul 1965a). On methylation analysis the acid degraded gum showed 2,4-dimethyl-D-galactose; 3,4,6-trimethyl-D-mannose; 2,3,6-trimethyl-D-galactose and 2,3,5-trimethyl-L-arabinose (3:1:2:trace) indicating a molecule of 1,6-linked galactose and 1,2-linked mannose residues (Farooqi 1970).

Acetone precipitated neem (*Azadirachta indica*) gum contained both carbohydrate and protein, which although inseparable by GPC, could be resolved by TEAE-cellulose chromatography into a number of fractions differing in the ratios of carbohydrate and protein (Narayan and Pattabiraman 1973). Pronase digestion of neem gum yielded a glycoconjugate which on ion-exchange chromatography showed the product to be a high M_r heteropolysaccharide, associated with a small amount of protein. A glycopeptide rich in D-glucosamine was also isolated from the column fractions, in which the aminosugar was linked to L-aspargine (Ramakrishna Nayak and Pattabiraman 1978).

The exudate gum from *Lannea coromandelica* was shown to contain D-galactose and L-arabinose (4:1) (Ramachandran and Joshi 1968). Structural analysis revealed a branched β-1,4-linked D-galactan.

In an attempt to find the dissociation constants of gum arabic and polyacrylic acids, an equation has been derived to account for the sol-concentration effect (Ghosh 1974).

Seed gums invariably represent the non-starchy reserve polysaccharides. An exhaustive screening of hundreds of plant species, mainly belonging to *Leguminoseae* family, for seed polysaccharides was undertaken by National Botanical Research Institute, Lucknow (Farooqi 1976; Farooqi *et al* 1984). On the basis of such studies the potential sources identified were *Cassia*, *Crotalaria*, *Indigofera*, *Sesbania* and *Desmodium*. The endosperm of many of the plant seeds contribute a rich treasure of galactomannan polysaccharides which have attracted enormous academic, industrial and technological attention (Dea and Morrison 1975). In general, these galactomannans have a backbone of β-1,4-linked D-mannose to which are attached single α-D-galactosyl stubs at 0–6 of certain mannosyl residues (figure 20). The various galactomannans exhibit variations in mannose to galactose ratio, nature of distribution of galactose along the mannose backbone, and DP of the polymer, and as a result, considerable variations in solubility and also gelling and functional characteristics are noticed.

Guar (*Cyamopsis tetragonolobus*) and locust bean (*Ceretonia siliqua*) galactomannans have received maximum attention due to their potentialities both in production and utilization. In fact guar gum was produced commercially as a replacement for locust bean gum. Much work has been done by several groups of workers all over the world on the isolation, purification, rheological characteristics and utilization of guar gum (Dea and Morrison 1975). Guar gum contains approximately twice as many α-D-galactosyl stubs as does locust bean gum.

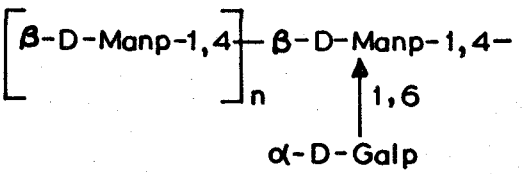


Figure 20. General structure of galactomannans.

Gum is present to the extent of about 35–42% of guar seeds. It is usually obtained by dry milling methods which are economical, although wet milling processes are reported. Recently, a simple wet milling method involving 2% $NaHCO_3$ at boiling temperatures for 5 min was employed for getting guar gum of good quality and recovery (Umadevi Sajjan 1984).

Using the guar galactomannan as a model compound, lectin mediated polysaccharide interaction, measured turbidimetrically, was demonstrated (Appukuttan *et al* 1984). The lectin was isolated from jack fruit (*Artocarpus integrifolia*) seeds. Turbidity of the lectin with soluble guar gum was abolished beyond pH range 4·5–9 and also in the presence of 0·5 M potassium thiocyanate or 1 M urea. By these inhibition experiments the specificity of lectin for the α-galactoside was clearly established.

There are a few galactomannans having structures that deviate from the classical type (Dea and Morrison 1975). The galactomannan from *Cassia absus* has mannose-galactose in 3:1 ratio (Kapoor and Mukherjee 1969, 1971, 1972). Structurally it is composed of ~85% of β-1,4-linked mannose and the rest are 1,3-linked; these in turn are substituted (50%) at 0–2 by α-D-galactosyl groups, and the rest of D-galactose are attached α-1,6 to the backbone. This structure bears similarity to those characterized from microorganisms (Gorin and Spencer 1968). By graded acid hydrolysis, 5 structurally important oligosaccharides were isolated by charcoal-Celite chromatography and characterized (Kapoor and Mukherjee 1972). One of them was identified to be 2–0-α-D-galactopyranosyl-D-mannose, which showed unambiguously the presence of 1,2-linkage in this galactomannan. The acid degraded gum (G-M* = 1:3) had a DP of 16, possessing the classical structure.

By employing classical methods and NMR spectroscopy the structure of the galactomannan from *Cassia alata* Linn. has been elucidated (Gupta *et al* 1984). The polysaccharide was found to be homogeneous by GPC. It had a M_r of ~26,400 and on hydrolysis it gave D-galactose and D-mannose in 1:2·7 ratio. PMR spectral data of the native polysaccharide and the derived oligosaccharides supported the chemical structure deduced. The α-anomeric nature of galactose was also ascertained by the precipitin reaction with a lectin from *Bandeiraea simplicifolia*, which is reported to be specific for α-D-galactosyl residues. In consonance with this, treatment of the polysaccharide with α-galactosidase cleaved quantitatively all the galactosyl residues, leaving behind a mannan-type polymer.

Partial hydrolysis of the polysaccharide from the seeds of *Caisas-Grandis* resulted in the isolation of 5 neutral oligosaccharides. Employing the classical methods the structures of these oligomers were established; particularly the tri- and tetrasaccharides had unusual structures (Bose and Srivastava 1978).

β-D-Galp-1,4-β-D-Galp-1,4-D-Man

β-D-Manp-1,4-β-D-Galp-1,4-β-D-Galp-1,4-D-Man.

The galactomannan obtained by 10% NaOH extraction of the kernel of the nut of green palmyra-palm (*Borrassus flabellifer* Linn.) contained G-M = 1:2·4 ratio (Mukherjee *et al* 1961). The polysaccharide was purified by copper-complexing

*G-M: Galactose—mannose ratio

method, and the α-linked galactose residues being more labile were partially cleaved during the acid treatment employed for dissociation of the copper complex. Some of the galactose residues could be hydrolysed even with 0·02 N oxalic acid. Therefore, during purification steps the G-M ratio of the polysaccharides varied from 1 : 2·4 to 1 : 3·4. However, their structures resembled that of guar gum.

A number of galactomannans possess chemical structures almost identical to that of guar gum. For example, galactomannans from the seeds of *Pheonix dactylifer* (G-M = 1 : 10) (Jindal and Mukherjee 1971), *Cassia fistula* (G-M = 1 : 4) (Kelkar and Mukherjee 1971), *Ipomoea muricata* (G-M = 1 : 1·8) (Khanna and Gupta 1967), *Sesbania grandiflora* (G-M = 2 : 3, chain length of 18–20 hexose units) (Subba Rao and Rao 1965), *Sesbania speciosa* (G-M = 1:2·2) (Venkateswara Rao *et al* 1980), *Desmodium pulchellum* (G-M = 1:2) (Sinha and Tiwari 1970), *Delonix regia* (G-M = 1:2) (Kapoor 1972), and coconut kernel (*Cocos nucifera*, G-M = 1:2) (Rao *et al* 1961).

The seed galactomannan isolated from *Ipomoea fistulosa* possessed a D-galactose: D-mannose ratio of 3 : 10. It had the usual structure (Gupta *et al* 1979a).

Germination studies of the seedlings of *Sesbania grandiflora* Pers. have revealed that the galactomannan occurring in the inner coat (tegmen) of the seeds serves as the major source of carbohydrate for the seedling to grow, particularly for the synthesis of sucrose (Subba Rao and Rao 1964). Comparative studies with other leguminous seeds have indicated the participation of the tegmen constituents in the biochemical activities of the seedlings of *S. grandiflora* seeds, but not of other seeds. In this instance the galactomannan, like starch, serves as reserve carbohydrate source.

The structure of galactomannans isolated from *Moringa oleifera* (exudate gum), *Sesbania aegyptica* (seed gum) and *Litsea polyantha* (leafy mucilage) were established by detailed structural studies (Banerjee *et al* 1984) including precipitin reaction with lectins from the seeds of *Artocarpus integrifolia* and *A. lakoocha* (Chatterjee *et al* 1982). Fragmentation analysis yielded 4 oligosaccharides, viz (i) 4-0-β-D-Manp-D-Man; (ii) 6-0-α-D-Galp-D-Man; (iii) 6-0-α-D-Galp-4-0-β-D-Manp-D-Man and (iv) 4-0-β-D-Manp-4-0-β-D-Manp-D-Man. The galactomannan from *S. aegyptica* has a DP of *ca* 35–38, and its G-M ratio being 1 : 1·7 (Bhattacharya *et al* 1983).

Two galactomannans have been isolated from *Cassia siamea* Linn. (Islam *et al* 1977) and *Cassia corymbosa* (Tewari *et al* 1984) and partially characterized. The former has galactose-mannose in 1 : 1·5 ratio and the latter in 4 : 7 ratio. Structural studies of the latter galactomannan have revealed a structure similar to that of guar galactomannan.

From the seeds of *Strychnos potatorum* Linn. a polysaccharide was isolated and partially characterized (Ram *et al* 1973). Some viscosity studies of the gum are also reported.

6.1b *Rheology*: Purified guar gum exhibits pseudoplastic behaviour, having maximum viscosity at pH 7–8. Above 0·75% it showed enhanced viscosity upon heating at 95°C for a short period and cooling to 30°C, indicating the aggregation of molecules. The gum was compatible with many salts, excepting sulfates of Na^+ and NH_4^+, which steadily decreased the viscosity. Sugars such as glucose, sucrose and maltodextrins increased the apparent viscosity, but decreased the pseudoplastic behaviour of gum. Purified guar gum showed enhanced water holding capacity, and

thus exhibited high thickening, good suspending, foam and emulsion stabilizing abilities. It delayed the onset of initial gelatinization and retarded the retrogradation of starch, at 0·5% level improved the texture of starch gels and inhibited synergesis upon ageing, probably indicating hydrogen bonding interactions between gum molecules and amylose chains (Umadevi Sajjan 1984).

A few rheological and functional characteristics of galactomannan from *Cassia occidentalis* (G:M = 1:3·6) (Wankhede *et al* 1984a) and *Sesbania aculeata* (G-M = 1 : 4·5) (Wankhede *et al* 1984b) have also been investigated.

Viscosity-wise the galactomannan obtained from *Caesalpinia pulcherrima* Linn. appeared to be better (4% dispersion resulted in a gel) than the locust bean gum. Preliminary nutritional studies of diets supplemented with *C. pulcherrima* galactomannan have also been made (Bains *et al* 1956).

6.1c *Modification*: A number of derivatives such as methyl, carboxymethyl, hydroxyalkyl ethers, succinates, benzoates, acetates and oxidized gum have been prepared from guar gum. The periodate-oxidized gum increased the dough stability and resistance to stretching but decreased the mixing tolerance index and water absorption (Umadevi Sajjan 1984). The effect increased with the increasing degree of oxidation. The carboxymethyl guar gum had a better water holding capacity, but with the increase in the degree of substitution water holding capacity decreased (Umadevi Sajjan 1984).

Some studies were done on the modification of guar gum by α-D-galactosidase (Umadevi Sajjan 1984). The enzyme was obtained from guar seeds germinated for 2–3 days. Treatment of native guar gum with α-galactosidase gave a product having a mannose to galactose ratio of 3·35 : 1 whereas the untreated gum had 1·65 : 1. The gum prepared from germinated guar seeds had a ratio 2·4 : 1. Unlike the native gum which did not gel the enzymically modified gum M : G ratio (3·35 : 1) formed a soft gel at 5°C, melting at 20°C. Preliminary studies indicated that gelling ability of galactomannan depends not only on the M : G ratio, but also on the arrangement of galactose side chain on the mannose backbone.

A gel chromatography medium has been prepared from guar gum cross-linked with epicholorohydrin in water-2-propanol system (Gupta *et al* 1979c). The degree of cross-linking was adjusted by the concentration of gum and cross-linking agent and solvent ratio. Two gels designated as guar gel 5-X 30 and 2-X 10 were prepared and their chromatographic evaluation (using a variety of inorganic, aromatic/heterocyclic compounds as well as amino acids) monitored (Gupta *et al* 1979b). For the two gels the M_r exclusion limits were ~ 15,000 and 70,000, respectively (for globular proteins). A cation exchanger (CM-guar, 5-X 30) and an acidic anion exchanger (DEAE-guar, 5-X 30) were also synthesized (Gupta *et al* 1979b).

From guaran, a new reagent 'blue guaran' was prepared by reacting it with monochlorotriazinyl reactive dye (Procion Blue HB) and used for quantitative estimation of lectins (Rathaur *et al* 1981). On adding the lectin solution to an aqueous solution of the blue guaran, dye-bound guaran is precipitated and the difference in absorbance of the resulting blue colour-complex before and after the lectin addition was proportional to the amount of lectin present in the sample. Thus, a simple colorimetric method of estimating the galactose-specific lectins was possible.

A boron-selective resin has been prepared by cross-linking of guaran (Bhatnagar

and Mathur 1977). Since galactose and mannose units in guaran contain a pair of *cis*-hydroxyl groups, the molecule undergoes reversible pH dependent gelling with boron. Cross-linking of guar gum with cyanuric chloride or epichlorohydrin gives an insoluble, water swellable polymer, retaining its ability to complex boron. The method is useful for the determination of boron, and comparable to the direct method.

6.2 *Mucilages*

6.2a *Chemistry and structure*: Mucilages are naturally occurring high M_r polysaccharides and are widely distributed in bark, roots, stems, leaves, fruits, flowers and seeds of plants (Tharanathan 1977). Mucilages can be extracted, depending upon the source of material, by different methods including extraction with water, dilute acids, aqueous alkalis and salt solutions, followed by precipitation with a miscible non-aqueous solvent, such as ethanol or acetone or by freeze drying (Tharanathan 1977).

Litsea polyantha plant grows abundantly in India. The highly viscous water extract of the leaves is used as a purgative/laxative in the indegenous system of medicine. The mucilaginous polysaccharide obtained by alcohol precipitation of the aqueous extract consisted of L-arabinose and D-xylose together with traces of D-glucose and D-galactose (Bhattacharya *et al* 1984). Cetavlon fractionation of the polysaccharide furnished precipitable and non-precipitable fractions, which were purified on Sephadex G-100. The two fractions consisted of arabinose and xylose in 4:1 and 2:1 mol ratios, respectively. Structurally they were arabinoxylans with arabinose as side chains in 1,2- and 1,3-linkages attached to a 1,4-xylan core.

The mucilage from *Savia aegyptica* seeds (tukhmulanga) is an efficient clarifier for sugar cane juice and finds use in paper, printing and textile industries, and in medicine as a emolient, diuretic and blood plasma expander. On hydrolysis the mucilage gave D-galactose, L-arabinose, L-rhamnose and D-galacturonic acid (Chatterjee and Mukherjee 1958). An aldobiouronic acid, 2-0-(D-galactopyranosyl uronic acid)-L-rhamnopyranose was characterized by the partial hydrolysis of the mucilage.

Deola (*Hibiscus ficulneus*) mucilage is composed of D-galactose, D-glucose, L-arabinose, L-rhamnose and traces of D-xylose (Bajpai and Mukherjee 1969). Partial acid hydrolysis gave an aldobiouronic acid similar to the one above. Structural studies of the native mucilage revealed it to be a rhamnogalacturonan having side chain residues of galactose linked 1,3 (Bajpai and Mukherjee 1971).

The genus *Ocimum* consists of many species found in tropical Asia, Africa and America. The seeds and leaves of these plants find extensive use in indigenous medicine (Nadakarni 1954). A systematic study has been carried out on the seed mucilages of different *Ocimum* species (Tharanathan 1977). The capsular mucilages of the seed of *O. canum* Sims (Anjaneyalu and Tharanathan 1971) and *O. basilicum* Linn. (Tharanathan and Anjaneyalu 1974) were extracted from water in 7 and 20% yields. On complete hydrolysis both the mucilages gave rise to D-glucose, D-galactose, D-mannose, L-arabinose, D-xylose and L-rhamnose in approximate proportions of 16:12:4:4:2:5 in *canum* (uronic acid content being 8·2%) and

25:25:10:15:15:5 in *basilicum* (uronic acid content being 7·3%). The latter were identified as D-galacturonic and D-mannuronic acids. Fractionation studies on *canum* mucilage gave a glucomannan (glucose and mannose ratio = 10:3) and a galacto-glucomannan (galactose, glucose and mannose in 2:4:1 ratio).

The acid-stable core polysaccharide (43% yield) isolated easily by mild hydrolysis of these mucilages was found to be a mixture of cellulose-like glucan and a glucomannan, having alternate glucose and mannose residues in 1,4-linkages (Tharanathan and Anjaneyalu 1975). The acidic polysaccharide obtained from these mucilages was shown to be a β-1,4-linked D-xylan, with side chains at 0–2 and 0–3 substituted by residues of D-galacturonic acid, rhamnose and arabinose in various linkages (Anjaneyalu and Channe Gowda 1979, 1980).

From *O. gratissimum* the mucilage was extracted in 14% yield (Tharanathan and Shamanna 1975). The seed mucilage was composed of 43·8% hexoses, 23·8% pentoses and 9·7% uronic acids. Fractionation studies yielded an arabinoxylan (1,4-linked) with 60% of the xylosyl residues substituted at 0–2 and 0–3 with 0-β-D-galactopyranosyl-1,3-L-arabinose, L-arabinofuranosyl or D-galactopyranosyl uronic acid side chains (Anjaneyalu *et al* 1983). These structural features for the polysaccharide accorded with periodate-oxidation data.

The homogeneous acidic polysaccharide (18% yield) obtained from the seeds of *O. adscendens* consisted of D-galactose (20%), D-galacturonic acid (35%) and L-rhamnose (39%) (Anjaneyalu *et al* 1984). Unlike other *Ocimum* mucilages, *O. adscendens* mucilage did not contain xylose. The seeds of the first 3 *Ocimum* species are black coloured and oval in shape; while those of *O. adscendens* are brown coloured and spherical. Structural studies indicated that the backbone of the polysaccharide to be →4)-GalpA-1,2-L-Rhap-(1→. Nearly two thirds of the rhamnopyranosyl units are 0–4 substituted by D-galactopyranosyl non-reducing end groups. A similar backbone structure is reported in the polysaccharides of mangle gum (Sarkar and Rao 1975).

From the Cetavlon non-precipitable fraction of *O. adscendens* mucilage a neutral polysaccharide was isolated by chromatography on DEAE-cellulose (Khan *et al* 1986). It was composed of L-rhamnose, D-galactose and L-arabinose (1:2:2). The polysaccharide possessed a 1,4-linked D-galactopyranose backbone with occasional side chains at 0–6 of 1,5-linked L-arabinofuranose terminating in rhamnopyranosyl residues. Such a structure is not frequently reported in arabino-4-galactans.

A significant feature of some of the *Ocimum* seed mucilages is the presence of O-acetyl groups, which seems to be interesting (Anjaneyalu and Tharanathan 1971). Secondly, the *O. canum* mucilage contained appreciable amounts of lipids, free and bound (Anjaneyalu and Tharanathan 1971). For quantitative recovery of free lipids prior hydration of the mucilage followed by extraction with highly polar solvents (like dioxan) was necessary. It appears that the free lipid fraction, the nature of which is unknown, may help the penetration of solvent molecules and hence influence the swelling power of the mucilage. In fact the defatted mucilage, unlike the native mucilage, had reduced swelling power and dispersibility in aqueous medium.

With regard to the seed characteristics, mucilage composition and main structural features of the major acidic and neutral polysaccharides, the taxonomic reclassification of *O. adscendens* in the *Becium* genus (Matthew 1983) seemed to be well supported. This species is now identified as *Becium filamentosum* (Forsskal) Chiov (Matthew 1983).

The mucilaginous jelly from *Aloe vera* leaves is a polysaccharide aggregate composed of glucose and mannose (1 : 1) together with 2·4% uronic acid, and 4 partially acetylated glucomannans, linearly 1,4-linked, differing in glucose to mannose ratio and O-acetyl contents (Channe Gowda *et al* 1979). The polysaccharide from *Aloe plicatilis* Miller is also a linear 1,4-linked glucomannan (glucose to mannose ratio, 1 : 2·8) (Hulyalkar *et al* 1956).

The mucilage extracted from the seeds of *Mimosa pudica* Linn. is widely used as suspending, emulsifying and tablet binding agent. The plant (also called *lajwanthi*) is a diffuse undershrub, and the leaves are exceedingly sensitive to touch. A decoction of the plant is used in gruel and also in medicine against urinary complaints. The seed mucilage is composed of D-xylose and D-glucuronic acid (5 : 1) and it has a highly branched structure (Baveja and Oberoi 1973).

Isabgul (*Plantago ovata* Forsk, psyllium) is grown in Gujarat and Rajasthan. Both seeds and husk contain a viscous mucilaginous polysaccharide, which has the property of absorbing large quantities of water, and is utilized in formulating bulk laxative. The major polysaccharide has been shown to be a highly branched acidic xylan (Kennedy *et al* 1979). The viscosity and a few rheological characteristics of this polysaccharide have been studied (Mittal and Zacharias 1971; Bandyopadhyay 1961).

The mucilage isolated from the tubers of *Asparagus racemosus* Willd. is shown to be composed of glucose and glucuronic acid in 3 : 2 ratio (Rao and Budhiraya 1952). An aldobiouronic acid (composed of glucose and glucuronic acid) was isolated by partial hydrolysis of the mucilage and partially characterized.

The mucilage from *Aegle marmelos* Correa contains a galactan and pentosan, which on acid hydrolysis gave galactose, arabinose and traces of O-methyl pentose (Parikh *et al* 1958).

Some preliminary studies were reported on the polysaccharides of *Phaseolus aureus* and *P. vulgaris* (Chakraborty and Rao 1969). Sequential extractions with cold and hot water and 0·1–1·0 N NaOH of the seed powder yielded a series of polysaccharide fractions varying in their sugar composition (Chakraborty and Rao 1969).

Extractions with cold and hot water and 0·1–1 N NaOH of black gram (*Phaseolus mungo*) gave 8 neutral polysaccharides and all of them contained major amounts of glucose together with small amounts of galactose and arabinose (Chakraborty 1975). In contrast extraction with acetate buffer (pH 4·6) followed by acetone precipitation gave a proteinaceous polysaccharide (3% N_2) containing galactose, arabinose, rhamnose and galacturonic acid (13 : 18 : 3 : 2) (Kadkol *et al* 1961). Amino acid analysis of the protein indicated the absence of sulphur-containing amino acids. On the basis of these results it was concluded that the black gram mucilage is a mucopolysaccharide containing ~20% protein (Kadkol *et al* 1961). Black gram is one of the legumes frequently used for preparing popular and typical Indian breakfast foods (Reddy *et al* 1982). Earlier, it was demonstrated that the soft, spongy texture of leavened food preparations such as the *idli*, *dosa*, etc which contain black gram, results from the cooperative functioning of the surface-active proteins and the highly viscogenic arabinogalactan present in the legume (Susheelamma and Rao 1979b). In an attempt to isolate a protein-free polysaccharide from black gram 10% TCA extraction was found to be the best way, the yield of polysaccharide was ~6% (Susheelamma and Rao 1978).

Subsequent detailed studies on this polysaccharide established its homogeneity,

nature of sugar constituents (L-rhamnose, L-arabinose and D-galactose in the ratio of 1:9:3, together with traces of xylose and D-galacturonic acid, 18·5%) and also the nature of glycosidic linkages (Ramadas Bhat *et al* 1987). As the native mucilage was only partly soluble in water, it was not amenable for further studies. Hence, the acidic native polysaccharide was carboxyl-reduced to a neutral polysaccharide, which was easily soluble in water. The latter contained rhamnose, arabinose and galactose (1:9:5). Structural studies on both native and carboxyl-reduced polysaccharides revealed a L-rhamno (1,2-linked)-D-galacturonan (1,4-linked) backbone appended by terminal as well as chain-linked residues of galactose and arabinose (highly branched side chains). This structure was supported by the isolation and characterization of a few acidic and neutral oligosaccharides derived by partial hydrolysis of the native polysaccharide.

Okra (*Hibiscus esculentus* L.) is a commonly used vegetable available almost round the year. The mucilage from fresh, tender okra pods find use as a plasma expander, clarifying agent, etc (Whistler and BeMiller 1973). Extraction of immature okra pods with 0·1 N HCl furnished in 1% yield a viscogenic mucilage rich in carbohydrates (with a protein content of 1·6%) (Ramadas Bhat and Tharanathan 1986a). The mucilage was highly soluble (over 80%) in 1% aqueous sodium borohydride solution but not in water. Precipitation with Cetavlon together with DEAE-cellulose chromatography gave 3 acidic polysaccharide fractions. Structural analysis of one of the homogeneous fractions revealed it to be a rhamnogalacturonan-type polysaccharide with galactose located at non-reducing terminals as single residues or as galactobiose side chains (Ramadas Bhat and Tharanathan 1986a). A few functional properties (such as viscosity, gelling, foam stability, etc) of the borohydride-soluble okra polysaccharide were also carried out (Ramadas Bhat and Tharanathan 1987).

Linseed (*Linum usitatissimum*), also called flax, is a commercial crop grown chiefly for the production of fiber from which linen is made, and of linseed oil which finds use in varnishes and paints. Linseed mucilage has varied applications in food, pharmaceutical and other industries (Whistler and BeMiller 1973). The mucilage could easily be isolated in 6% yield by aqueous extraction and alcohol precipitation (Muralikrishna *et al* 1987a). It consists of L-rhamnose, L-fucose, L-arabinose, D-xylose, D- and L-galactose, D-galacturonic acid in 24:8:9:17:21:4:17% ratio.

The mucilage consisted of two homogeneous fractions (Muralikrishna *et al* 1984). The neutral fraction was a highly branched arabinoxylan (β-1,4-linked xylose in the backbone to which are attached galactose and part of xylose and arabinose moieties as non reducing terminals; whereas the remaining arabinose is present in 1,3-linkage). It has a M_r of 480,000 (Muralikrishna *et al* 1987a). The structure of the acidic polysaccharide was elucidated to be L-rhamno-D-galacturonan, with a M_r of 575,000 (Muralikrishna *et al* 1987a). Some functional properties of the total mucilage were also studied (Muralikrishna *et al* 1984, 1987b; N S Susheelamma, unpublished results).

From defatted coffee powder polysaccharides were extracted (0·5 and 1·5% yield) with 2 N HCl at room temperature for 6 h followed by alcohol precipitation (Shadaksharaswamy and Ramachandra 1968b). *C. arabica* contained rhamnose, arabinose, mannose and galactose in 10·3:30·7:29·5:19·2 ratio, whereas that from *C. robusta* had these sugars in 9·9:30·3:26·3:18·8 ratio, respectively.

From the seed coat of *Hyptis suaveolens* a mucilage was isolated, which

contained L-fucose, D-xylose, D-mannose, D-galactose, D-glucose and 4-0-methyl-D-glucuronic acid (1:2·5:1·5:7:12·5:1) (Channe Gowda 1984). Two fairly pure fractions were obtained by complexing with Fehling's solution. The neutral fraction had D-mannose, D-galactose and D-glucose (1:4·5:7·5) and the acidic fraction had L-fucose, D-xylose and 4-0-methyl-glucuronic acid (1:2·5:1·1).

Some progress has been made on the IR spectral characteristics of a few aldobiouronic acids isolated from plant gums and mucilages (Bajpai *et al* 1970). The mixture of sugars were resolved by cellulose column chromatography and individual fractions identified by PC. Barium salts of the aldobiouronic acids were prepared and IR spectra recorded. Two distinct bands at 1590–1575 and 1460–1420 cm^{-1}, corresponding to vibrations of the carboxylate ion were noticed. In addition, several other changes in the spectra were observed.

Fenugreek (*Trigonella foenum-graecum*) is a spice used in South Indian cooking, in addition to its use as wet-end additive, for soft wood kraft and sulfite finishes. The mucilage from fenugreek seeds is usually contaminated with protein, which is removable by repeated dissolution in water and reprecipitation with alcohol or saturation with $MgSO_4$. The purified mucilage was reported to be galactomannan (Chatterjee *et al* 1982). The CrO_3-oxidation and serological cross reaction with several lectins were performed on this galactomannan suggesting that all the D-mannose residues are β-linked and D-galactose, present at non-reducing end groups are α-linked (Chatterjee *et al* 1982).

Mucilaginous polysaccharides have been isolated (13·2% yield) by cold acidified water extraction of a *Phaseolus glabra* meal (Sinha 1960a). The crude material on acid hydrolysis showed xylose, arabinose, galactose and galacturonic acid. Similar extractions of *Pongamia glabra* gave a complex mucilage composed of arabinose, galactose, xylose, rhamnose and galacturonic acid (Sinha 1960b).

From buck wheat a mucilaginous polysaccharide has been extracted (10% yield) with acetate buffer of pH 4·6 and precipitated with acetone. On acid hydrolysis it showed glucose, galactose, arabinose, xylose and rhamnose (CFTRI Report 1962–63).

6.2b *Structure-function characteristics*: The mucilaginous polysaccharide of black gram exhibits excellent gas-holding and dough raising properties of special significance in the texture of leavened food products. The viscogenic nature of the polymer seems to be responsible for such a functional property (Susheelamma and Rao 1979b). A few other polysaccharides with dissimilar structures were also shown to possess foam-stabilizing property (Ramadas Bhat 1987). To understand this at the molecular level a kinetic study of the mucilage reduced to different extents was compared with the foam stabilization property. It was found that as the content of uronic acid diminished (18·5% in the native mucilage to ~1% in fully reduced polysaccharide) the solubility of the product increased and the viscosity decreased. Interestingly, the foam stabilizing property of the reduced polysaccharides also decreased steadily and finally disappeared (Ramadas Bhat *et al* 1987). It is therefore very probable that the uronic acid carboxyls in the native polysaccharides are at least partly responsible for its viscosity and as a result exhibits the characteristic functional property.

Due to synergistic interactions, a blend of black gram starch and mucilage showed additive foam stabilizing effect (Muralikrishna *et al* 1987b). Due to its higher water

absorption the mucilage showed improved dough characteristics and strengthening effect on soft wheat dough (Muralikrishna *et al* 1987b).

In a separate study it was shown that the viscogenic property of the native black gram polysaccharide varies considerably depending upon the conditions of extraction, such as the concentration of TCA used, duration and temperature of extraction (R N Tharanathan, unpublished results). Black gram is usually used in a variety of preparations and it is likely that the specific functional property, the composition and chemical structure of the polysaccharide may also vary depending upon a particular preparation. Our preliminary findings are in favour of this (R N Tharanathan, unpublished results).

Some information on the effect of simple processing on the properties of black gram protein and polysaccharide is available (Susheelamma and Rao 1979a). Overnight fermentation of the batter from black gram did not adversely affect the functional properties of either the protein or the polysaccharide. Seeds stored in the sealed containers in cold retained the functional properties. However, an optimum soaking time of 10–12 h was necessary as soaking (the *dhal*) for longer periods (18–20 h) decreased the viscosity of the polysaccharide. Similarly, heat treatment drastically affected the functional properties.

6.2c *Applications*: Both gums and mucilages, either in their native or modified form find extensive applications in various food and non-food industries. They are, therefore, the carbohydrates of commerce having a tremendous export potential. Basically they exhibit excellent thickening power in aqueous systems and as a consequence show very desirable rheological characteristics. Their usage in consumer products range from increasing viscosity in food products to preventing the redeposition of soil in detergents. Polysaccharides are useful as thickening agents as they increase the resistance to flow of a liquid, they provide body, mouthfeel and texture to prepared foods (Saxena 1965; Sanford 1983).

Gums exhibit, in addition, secondary functions such as emulsification, suspension stabilization, encapsulation, flocculation, film forming, binding and coating properties. These functional attributes are important in controlling the texture of foods as well as their flavour, appearance and colour. However, because of wide range of functional characteristics exhibited by these polysaccharides and variations in operating and processing conditions, combinations of gums (or polysaccharides) are often used to obtain a desired functionality.

The use of guar gum upto 1% level in wheat flour has shown improved bread making quality, particularly improvement in water absorption capacity of dough, bread yield, crumb softness and appearance of crust (Venkateswara Rao *et al* 1985). Above 1% level the dough handling properties were adversely affected.

7. Hemicelluloses

The term 'hemicellulose' refers to an ill-defined but distinct group of polysaccharides. It covers a broad group of structural polysaccharides occurring in close association with cellulose in the plant cell walls (Brillouet 1982). Invariably hemicelluloses are found associated with lignin, a highly complex polymer of phenylpropane residues. The intimate association with lignin hinders its quantitative isolation. In general

hemicelluloses may be isolated free of cellulose by extraction of the delignified plant material with dilute alkali (4–15% NaOH), preferably in an oxygen-free atmosphere (Whistler and Feather 1962). Hemicelluloses are further classified on a solubility basis into A, B and C groups (Whistler and Feather 1962). The nature of the constituent sugars in hemicellulose group of polysaccharides varies according to the source. Pentose polysaccharides are preferentially precipitated as hemicellulose A leaving behind the more soluble pentosans and hexosans in solution which are collectively designated as hemicellulose B (and C).

7.1 *Chemistry and structure*

One of the most important of these polysaccharides is the xylan group, found invariably in lignified tissue of higher plants (Wilkie 1979). Xylans from a wide variety of sources possess very similar backbone structures (1,4-linked) but differ from one another in the number and nature of the side chain residues attached at 0–2 and 0–3. Accordingly, xylans of plant origin have been classified into 4 groups (Wilkie 1979), viz (i) homoxylans, composed essentially of D-xylose residues in either linear or branched structure; (ii) xylans containing arabinose residues, generally referred to as arabinoxylans are usually present in cereal grains and possess a α-1,4-linked xylan backbone substituted at 0–3 by L-arabinofuranose residues, the relative proportion of these side chains varies widely from source to source; (iii) acidic xylans containing 1,2-linked 4-0-methylglucuronic acid side chains, usually designated as 4-0-methylglucuronoxylans; and (iv) those from soft woods, in which linear 1,4-xylan backbone is substituted by both arabinose and 4-0-methylglucuronic acid side chains and are called arabino-(4-0-methylglucurono)-xylans.

Hemicellulose fractions isolated from pineapple leaf fibers mainly consisted of D-xylose, 4-0-methyl-D-glucuronic acid, and small amounts of arabinose, glucose, mannose and galactose (Sharma 1981). On partial hydrolysis, the 4% NaOH-soluble fraction yielded several oligosaccharides. The acidic disaccharide, obtained in good yield, was characterized as 2-0-(4-0-methyl-α-D-glucopyranosyluronic acid)-D-xylose, and showed structural similarity with that of jute fibers.

Extensive work has been carried out on polysaccharides of rosella (*Hibiscus sabdariffa*) (Gupta 1961) and sisal (*Agave sisalana*) (Gupta and Mukherjee 1967) fiber. On extractions with NaOH and alkaline borate solutions both the fibers afforded 4 fractions each. Fraction 2 from both of them had M_r of ~23,000. The DP of the rosella fraction 2 was ~124, whereas that of sisal fraction was ~109. Both were composed of 1,4-linked β-D-xylopyranose residues, approximately every 6th residue was carrying at 0–2 a terminal 4-0-methyl-α-D-glucuronic acid. Methylation data thus indicated some branching. Similar structural features were reported for *Agave americana* fiber (Banerjee *et al* 1965). The *Agave* hemicellulose fraction had a M_r of $4{\cdot}12 \times 10^5$, as indicated by light-scattering studies. Partial hydrolysis of the hemicellulose resulted in the isolation and characterization of a disaccharide, D-glucuronic acid-1,2-D-xylose.

D-Xylose (87%) and D-glucuronic acid (13%) were the major constituents of the hemicellulose extracted from the chlorite holocellulose of sabai grass (*Eulaliopsis binata*) (Guha *et al* 1973). Detailed studies indicated that the polysaccharide had contiguous residues of 1,4-linked D-xylose with single unit branches of D-glucuronic acid attached to one out of every 9 D-xylose units by a 1,2-linkage.

Purified hemicelluloses from the trunk of a young bael tree were isolated with 0·25 M NaOH (Basak *et al* 1982) and from the leaves of *Sansevieria trisfasciata* with 4% NaOH (Sharma and Mukherjee 1981). The polysaccharides contained D-xylose and 4-methylglucuronic acid in 1:6 and 5:1 ratio, respectively, with traces of other sugars. Structural studies revealed them to be a 1,4-linked D-xylan having branches of D-xylosyl and 4-0-methylglucuronosyl residues on some of the 0–2 of the main chain. Partial hydrolysis of the *trisfasciata* hemicellulose gave several oligosaccharides consisting of xylose and 4-0-methylglucuronic acid in 1:1 and 2:1 ratio, respectively (Sharma and Mukherjee 1982).

The principal hemicellulose of the floss of *Calotropis giganta* is a 4-0-methyl-D-glucurono-D-xylan with 12% uronic acid residues still attached to 0–2 of some D-xylose residues in the main chain (Channe Gowda and Anjaneyalu 1980).

A number of agricultural wastes/residues have been utilized in various industries for the manufacture of a variety of materials, which by themselves are useful or may be further converted to useful products. As a prelude to this, knowledge of the overall chemical make up of the residue is essential. With this in view, the nature of carbohydrates of groundnut shell polysaccharides were investigated in some detail (Radhakrishnamurthy and Srinivasan 1957a). Hemicelluloses were the major constituents (26%) of groundnut shells. Preliminary fractionation with glycerol-copper sulfate gave a series of polysaccharide fractions composed mainly of xylose, arabinose and uronic acid. A few fractions contained, in addition, rhamnose and/or galactose. Structural analysis of hemicellulose A (xylose-arabinose-glucuronic acid 92:0·4:5·4 ratio) (Radhakrishnamurthy and Srinivasan 1957b) and hemicellulose B (xylose-arabinose-glucuronic acid, 21:1:1) (Radhakrishnamurthy and Srinivasan 1959) showed 1,4-linked β-D-xylopyranose backbone having at 0–2 side chain stubs of non-reducing terminal D-glucuronic acid residues.

Two homogeneous hemicellulosic components, a highly branched xylan and a linear glucomannan were isolated from defatted groundnut flour in 0·5 and 3·5% yields, respectively (Wankhede *et al* 1979c). Methylation data on the xylan indicated a β-1,4-linkage with little branching at 0–2. Interestingly this xylan was devoid of any other sugar moieties. The glucomannan was similarly shown to be β-D-1,4-linked linear molecule. The results however suggested the fraction to be an aggregate of true glucomannan and a glucan or degraded cellulose (Tharanathan *et al* 1979).

Hemicelluloses were also isolated from defatted seeds of two varieties of sesame (*Sesmum indicum*) (Wankhede and Tharanathan 1976). White sesame contained 0·6 and 2·0% and black sesame 2·3 and 2·6% respectively, of hemicellulose A and B. In both the cases hemicellulose A consisted of glucose and galacturonic acid, and hemicellulose B was composed of glucose, arabinose, xylose and galacturonic acid. The presence of glucose in the latter was interpreted as due to the contaminating cellulose fraction. As in the flax and mustard seeds, these polysaccharides (or mucilages) contain colloidally dispersed cellulose solubilized in some fashion by the associated hydrophilic polysaccharides (hemicelluloses) (Smith and Montogomery 1959). It is claimed that this solubilization might occur by the noncovalent encapsulation of the cellulose by the associated polysaccharides (Smith and Montogomery 1959).

Lignin-xylan ester linkages play an important role in the acidity of the raw and demineralized fibers. Treatment of jute (*Corchorus capsularis*) fiber with aqueous potassium borohydride afforded a product containing 77% of the original lignin and

a water-soluble lignin-carbohydrate complex (Das *et al* 1981). The latter on hydrolysis yielded a new sugar 4-0-methylglucose in admixture with the original sugars. Alkaline extraction of the holocelluloses prepared from the original and modified fibers afforded crude xylans, which on fractionation with aqueous barium hydroxide solution yielded two pure D-xylans containing 15·9 and 10·5% uronic acid residues. The results indicated that ~34% of the acidic side chains of the xylan are linked to lignin.by an ester linkage. In a subsequent investigation (Das *et al* 1984a) on the origin of the acidity of the jute fiber the pH neutralization curves furnished by the raw and dimineralized fibers consisted of only one inflection point and both were found to possess remarkable dissimilarity compared to that furnished by the native D-xylan. The former curve resembled that of very weak acids and the latter that of weak acids.

Similar studies on masta (*Hibiscus cannabinus*) fiber gave a fiber containing 8·2% lignin. The OAc groups (10%) present in the fiber showed a characteristic IR spectrum at 1730 cm^{-1}. Delignification followed by repeated borohydride treatments of the fiber resulted in incomplete reduction (~25%) of the 4-0-methylglucuronic acid to 4-0-methylglucose (Das *et al* 1984b). Comparison of the nature of the neutralization curves prepared by titrating raw, dimineralized and cation-free saponified fibers and the pure D-xylan derived from the untreated fiber suggested that all the acidic side chains are ester bonded with lignin in the native state. The fiber underwent a coupling reaction with diazonium salt establishing the existence of free phenolic groups, and therefore acidity of the native fiber.

A glucomannan from sun hemp (*Crotalaria juncea* Hemp.) fiber was isolated by fractionation of the alkali-soluble hemicelluloses (Gupta *et al* 1976). It had an $[\alpha]_D$-45° and on acid hydrolysis yielded glucose, mannose and xylose in 1·2 : 1 : 0·7 mol ratio. Methylation data indicated 1,4-linked β-D-glucopyranosyl and D-mannopyranosyl residues. Some of the mannose (13%) and glucose (8·7%) are present as non-reducing end terminals.

A hemicellulosic xylan was isolated by 10% NaOH extraction of guar seed husk (Umadevi and Salimath 1986). The polysaccharide consisted mainly of D-xylose. It was a linear 1,4-linked xylan. On partial acid hydrolysis xylose and 4 homologus oligosaccharides were recovered and partially characterized.

Two amyloid-type fractions were isolated from field bean hulls by 10% NaOH extraction followed by acetylation, solvent fractionation and deacetylation (Salimath and Tharanathan 1982c). The major chloroform-insoluble fraction and the minor chloroform-soluble fraction were found to be homogeneous by various techniques. The polysaccharides contained xylose and glucose in various proportions. Detailed structural studies including oligosaccharide analysis indicated a new type of structure for the major fraction (xylose-glucose ratio of 1·9 : 1) in that it had a backbone of 1,4-linked D-glucose residues interspersed with single or multiple residues of 1,4-linked D-xylose. Some single side chain D-xylose units are attached at 0–6 of some glucose moieties (figure 21). In contrast, the minor fraction (xylose-glucose ratio, 3·7 : 1) had a backbone of 1,4-linked D-xylose interspersed with 1,4-β-D-glucose and having D-xylose side chains at 0–6 of glucose. The third fraction was found to be a mixture of linear 1,4-D-glucan and 1,4-D-xylan. The chemical structures of field bean xyloglucans are quite unusual and significantly different from the classical structures. Unlike the latter (Stephen 1983), which invariably contains side chain residues of fucose and galactose, field bean xyloglucan has none. However,

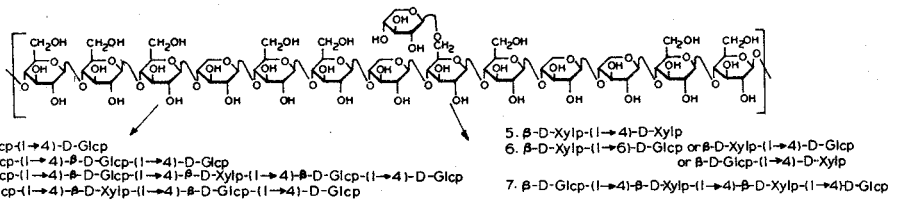


Figure 21. Structure of xyloglucan (fraction 1) and a few oligosaccharides.

like any other amyloid, field bean xyloglucan also gave positive starch-I_2 test, and the colour yield was significant and comparable.

Thus far xyloglucans, present in the endospermic tissues of various plant materials, have been regarded as reserve as well as structural polysaccharides. The latter function of particular value during seed dormancy is supported by germination studies. Except in rape seed (Aspinall *et al* 1977), there are no reports about their occurrence in hulls. It is hard to speculate at present on the biological role of this unusual polysaccharide in field bean hulls.

The homogeneous neutral polysaccharide obtained from bael fruit pulp contained arabinose, galactose and glucose (2:3:14). Structurally it was a 1,4-linked polymer having a variety of side chain branches (Basak *et al* 1981).

From black gram husk and endosperm various non-starchy polysaccharides were isolated and compositionally characterized (Ramadas Bhat and Tharanathan 1986a). Husk was rich in NSP of cellulosic (76%) and pectic (12%)-types; whereas starch was the major carbohydrate (40%) of the endosperm. Conspicuously xylose was absent in all the hemicellulosic fractions of the endosperm. The presence of significant amounts of arabinose in the pectic fractions of the husk indicated the probable existence of an arabinan-type polysaccharide in it.

Hemicelluloses have also been extracted from different pulses and cereals and compositionally characterized (table 6).

Proximate chemical composition of 8 varieties of *Leucaena leucocephala* (subabul) seeds is available (Arora and Joshi 1985). On dry weight basis the seeds contain protein 16–28%, fiber 30–35% of which cellulose is 3–10·9% and hemicellulose is 10–21%, and lignin 12–18%. The seeds contain 20–25% galactomannan-type polysaccharide which is used as a laxative.

The pentosan content of wheat was 27·7–39·6% and it appears to be associated with protein and polyglucosan fractions. When added at 2–3% levels to semolina, the mixing time and the dough stability increased. Thus, as evaluated by the farinographic technique the rheological properties of wheat dough were altered (Bains and Irvine 1965).

Arabinose, xylose, glucose and galactose were the major sugars of NSP of germinated bajra and ragi. Although the change (between the original and germinated samples) in arabinose to xylose ratio was marginal, the change in pentose to hexose ratio was significant on germination (Bhatia *et al* 1974).

NSPs of cereals and millets have a role to play in the texture or consistency and haziness of beer, i.e. in brewing (Venkatanarayana 1984). The alcohol-insoluble residue of the wort prepared from ragi contained mainly glucose with trace quantities of fucose, rhamnose, xylose and arabinose. Whereas that from a

Table 6. Carbohydrate composition (%) of hemicellulose A(1) and hemicellulose B(2) isolated from various legumes.

	Bengal gram		Horse gram		Cowpea		Black gram		Field bean		Winged bean	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Endosperm												
Yield	1·9	5·5	8·6	5·5	1·5	5·1	5·7	2·6	6·1	0·6	0·5	0·9
Rhamnose/fucose	tr	8·2	tr	—	tr	—	16·0	9·3	1·4	—	—	—
Arabinose	11·7	41·0	8·2	24·1	8·4	23·8	63·3	63·2	3·2	4·7	3·4	tr
Xylose	tr	—	tr	4·8	—	4·8	—	—	1·9	2·3	35·3	6·2
Mannose	—	—	—	—	—	—	—	—	9·0	—	—	—
Galactose	23·4	—	—	14·4	84·5	14·3	16·0	20·0	7·4	16·4	—	—
Glucose	58·6	41·0	82·0	48·1	—	47·6	—	—	75·9	68·2	60·8	93·7
Uronic acid	6·3	9·7	9·8	8·6	7·1	9·6	4·8	7·5	1·6	8·4	—	—
Husk												
Yield	1·2	13·2	10·9	0·1	10·6	0·5	10·9	2·6	7·5	2·7	ND	ND
Rhamnose/fucose	tr	—	tr	—	tr	—	60·4	15·4	—	—	ND	ND
Arabinose	24·9	15·7	6·3	33·3	11·2	15·3	7·2	9·4	—	4·0	ND	ND
Xylose	14·9	31·4	63·5	10·0	56·0	30·7	24·8	23·3	38·6	25·6	ND	ND
Mannose	—	9·4	—	3·3	—	11·5	—	—	—	—	ND	ND
Galactose	—	12·6	—	16·6	—	11·5	2·7	35·7	—	—	ND	ND
Glucose	49·7	22·0	25·4	26·6	28·0	23·0	—	—	54·1	70·3	ND	ND
Uronic acid	10·5	8·9	4·8	10·2	4·8	8·0	4·8	16·2	7·3	0·2	ND	ND

combination of ragi-barley malt and barley malt worts had xylose, arabinose and glucose in 1 : 1 : 5 and 1 : 1 : 4 ratios, respectively. The carbohydrates of beers indicated that the hydrolysates of non-fermentable carbohydrates consisted of arabinose, xylose and glucose (1 : 1 : 4 and 1 : 1 : 5) with traces of fucose and rhamnose (Venkatanarayana 1984).

NSP of 20 varieties of sorghum were also analysed (Chandrashekhar 1985). The water-soluble carbohydrates constituted about 1%, and this comprised pectin, pentosan and hexosan-type polysaccharides. The water-insoluble components were about 5% and cellulose 1%. Maximum variations were observed in the nature of pectic substances.

The unavailable carbohydrate of commonly consumed Indian foods has been determined by the recent Southgate method (Kamath and Belavady 1981). Amongst cereals, rice had the lowest (8·3%) and pearl millet the highest (20·3%), whereas sorghum, wheat and ragi had intermediate values. The crude fibre content of rice was 0·2% and that of pearl millet 1·2%. In the case of legumes, green gram had the lowest (15·2%) and Bengal gram the highest (25·6%); black gram and red gram were intermediate. Generally pulses had larger amounts of unavailable carbohydrates than any cereal except pearl millet. The estimated range of values (g $100\,g^{-1}$ of the edible portion of the food) for unavailable carbohydrates were: in roots and tubers, 3·5–7·9%, peanut varieties, 5·4–6·8%; green leafy vegetables, 2·9–4·0%; other vegetables, 0·4–6%; and fruits, 2·2–2·7%.

Some preliminary studies have been carried out on the role of NSP of red gram and their influence on dehulling characteristics (Ramakrishnaiah and Kurien 1985; P V Salimath, unpublished results). The various fractions such as the water-soluble and water-insoluble NSPs and the cellulosic fraction were isolated and analysed for their constituent sugars (pentoses, hexoses and uronic acids). It was reported that good dehulling varieties had relatively lower content of water-soluble NSP, which in turn contained lower levels of uronic acids.

The carbohydrates of arecanut have been fractionated into soluble and structural carbohydrates (CFTRI Report 1962–63). The 70% alcohol-soluble sugars were identified as sucrose, glucose and fructose. The polysaccharide on hydrolysis showed a complex mixture containing glucose, galactose, mannose, xylose and arabinose.

Polysaccharides have been isolated from paddy by extraction with 0·5 N NaOH at 30°C for 18 h (Kurup and Vijayagopala 1975). They were reported to be useful for treating atherosclerosis.

By extraction with 5% KOH the main hemicellulosic constituents of bamboo (*Dendrocalamus strictus*) were isolated (Negi *et al* 1970). Detailed studies carried out on this polysaccharide indicated a 1,4-β-D-xylan containing one D-glucuronic acid attached at 0–2 to every 9th xylopyranosyl unit.

Extraction with 10% NaOH of seeds of *Strychnos potatorum* furnished a polysaccharide composed of galactose and mannose in 11 : 1 molar ratio (Venkata Rao and Venkateswara Rao 1979). Structural studies revealed it to be a mannogalactan having a 1,4-linked D-galactose in the backbone which is substituted at 0–3 by single residues of D-mannose.

A mannan was isolated by extraction with 18% NaOH of kernel of palmyra palmnut and structurally analysed to be 1,4-linked molecule having $\sim$10% of side chain branches through 0–6 (Rao and Mukherjee 1962).

From pea skin (*Pisum sativum*) hemicellulosic polysaccharides have been extracted by 4% NaOH and purified by copper complexing (Banerji and Rao 1963a). The polysaccharide was composed of D-xylose and L-arabinose (5:1). Methylation analysis indicated a 1,4-linked D-xylan backbone having about 20% side chain arabinosyl units (Banerji and Rao 1963b).

7.2 *Biochemistry*

It was observed earlier during our studies on the extraction of protein from defatted ground nut flour (GNF) that the recovery of protein was only 60–70%, the rest being associated, probably by protein-carbohydrate (hemicellulose and/or cellulose) interaction in the residue (Tharanathan *et al* 1979). A complete extraction of protein from GNF is likely to be more economical and desirable as currently more and more protein isolates may be increasingly used in the manufacture of food beverages, high protein biscuits, weaning foods and various confectionaries. Some attempts were therefore made on the enzymatic digestion of GNF and look for protein extraction.

A hemicellulase preparation from a soil fungus belonging to *Fusarium* species was partially purified by conventional methods (Wankhede *et al* 1981). The enzyme showed optimum activity at pH 5–6 and 37°C. Both groundnut and sesame hemicellulose B were degraded to a considerable extent by the enzyme, whereas the purified glucomannan and xylan fractions of groundnut were hydrolyzed to a less extent. On treating the defatted GNF with the enzyme followed by protein extraction, it was found that the protein recovery was significantly higher (~90%) and the content of pentosans in the residue was low. The results clearly showed that the removal of pentosans had advantages for a more complete extraction of protein.

The crude glycoprotein obtained from bael tree seeds was resolved into 4 pure fractions (Mandal and Mukherjee 1981). Fraction 1 contained galactose, glucose, arabinose and rhamnose in 6:2:8:3 mol ratio. Its structure was deduced to be containing a β-1,3-linked galactan backbone having branches at 0–6 of glucose, arabinose and rhamnose in various linkages. The carbohydrate moiety is attached to the protein through threonine.

7.3 *Conformational studies*

Much work has been done on the conformational characteristics of oligo- and polysaccharides (Rao *et al* 1971; Satyanarayana and Rao 1970; Veluraja and Rao 1984). A variety of hemicellulosic fractions have been studied and useful data about their tertiary structures reported. It is well documented that some of the changes in properties and behaviour are attributable to water-macromolecular interactions. These in turn stabilize or disrupt the secondary and tertiary structures and alter the properties, such as their ability to form gels, etc. It is therefore necessary to understand, in terms of molecular structure, how chain molecules can interact in 3 dimensions to impart various physical and biological properties to macromolecules.

7.4 *Processing studies*

Some work has been reported on the nature of NSP of native and malted millets (Malleshi *et al* 1986a). A significant increase in the water-soluble NSP, a slight

decrease in hemicellulose A, but a marked increase in cellulose-type fractions were observed in malted millets. The water-soluble NSP fractions from native millets contained higher proportion of pentoses than hexoses, but malted millet fractions contained more hexoses than pentoses. Considerable amount of protein was found associated with all the fractions. The sugar composition of the hemicellulose B did not change much on malting. Due to the incomplete extraction of hemicellulose(s) the cellulose-type fraction still contained considerable amounts of arabinose and xylose, in addition to glucose. The alterations in the content and the composition of NSPs during malting is due probably to the depletion of embryo and starchy endosperm to meet the requirement of seed, and also due to the synthesis of new cell wall materials. This explains the slight increase in the cellulose-type material after malting. The increase in free sugar content of malted samples was at the expense of hydrolysed starch.

8. Dietary fiber and nutrition

Much has been reported about the pros and cons of dietary fiber. Dietary fiber is defined as the structural components (such as soluble polysaccharides/gums, pectins, hemicelluloses, cellulose and lignin) of plants present in the cell walls of leaf, stem, root and seed, that are ingested as part of the diet and are resistant to secretions of the human gastrointestinal tract (Southgate 1982). On the other hand crude fiber by definition is the material left after treatment with hot acid or alkali which is a method of fiber analysis. The quantity of these components vary with variety, processing and agronomic conditions. The characteristic property of fiber components is their enormous water-absorbing capacity, which in turn exerts several beneficial effects, such as increased stool bulk and decreased transit time, relieving the symptoms of diverticulosis and in some cases even obviating the need for surgery, exerting hypocholesteremic effect and reduction of incidence of ischaemic heart disease, and stimulation of strong insulin response and therefore deterring the onset of diabetes (Southgate 1982). However, of late questions have been raised about the binding of certain minerals as well as bile acids by ingestion of large quantities of fiber. It may also decrease the availability of such minerals as calcium, zinc, iron, copper and magnesium.

A number of studies have been made on the nutritional merits and demerits of unavailable carbohydrates of legumes and cereals. Incorporation, to the extent of 20%, of native and microcrystalline cellulose to a casein diet resulted in a gradual decrease of the productive energy of the diet (Shurpalekar *et al* 1971). A significant reduction in serum cholesterol content as well as phospho- and total lipid contents was also noticeable (Sundaravalli *et al* 1973). Increased plasma and liver cholesterol induced by cholesterol feeding could be largely counteracted by the concurrent feeding of cellulose (20%) (Sundaravalli *et al* 1971). This hypocholesterolemic effect was largely attributable to the increased excretion of bile acids in the feces of rats.

Faecal excretion of isolated carbohydrate fraction of field bean and ragi showed the following trend in increasing order-starch, pectin, hemicelluloses and cellulose (Saraswathi and Shurpalekar 1983). Whole field bean/ragi, however, induced a higher excretion of faecal nitrogen. The effect of reconstituted field bean obtained by mixing the various carbohydrate fractions was similar to that of the original. Calcium absorption was significantly decreased in the whole field bean only.

In vivo digestibility of the carbohydrates of red gram and Bengal gram was significantly less than that of corn starch (experimental control), whereas the carbohydrates of black gram and green gram were more digestible (Shurpalekar *et al* 1979). The caecal volume and faecal bulk of the rats were greatly increased with the diets containing legume carbohydrates. Incorporation of carbohydrates, prepared from different legumes as a sole source of carbohydrate in the diet, promoted a growth rate comparable to that by corn starch. The per cent nitrogen retention was not adversely affected.

Some information is also available on the beneficial effects of feeding ragi husk, native or treated, to experimental animals (Kanchana and Shurpalekar 1984). Pronase treatment brought down the husk protein content from 18 to 5%, and destarching (by glucoamylase digestion), however, increased the net protein content. The results indicated that part of the husk protein is utilizable by the rats for the improvement in growth. Further studies showed the involvement of the acid resistant hemicellulose fraction in such effects (Kanchana 1985). It also helped to increase the absorptive surface area of small bowel and villus height.

The extent of hydrogen production by cooked black gram seeds and cotyledons, germinated black gram seeds and a black gram and rice fermented-steamed product (*idli*) was investigated with rat bioassay method (Reddy *et al* 1980). Maximum hydrogen formation was from 60% cooked black gram cotyledons in the diet. The other two produced significantly lower flatus.

9. Cellulose

Cellulose is the most abundant and easily renewable organic material found in nature. It is principally a structural material, helping to preserve and protect the shape of the plant cell. Structurally cellulose is composed of D-glucopyranose residues condensed head-to-tail through β-1,4-glycosidic linkages to form long, unbranched chains (figure 22) (Rees 1967).

The characteristic properties of cellulose such as its high strength and its fibrous nature, inertness and insolubility all depend on the overall shape of the molecule. Extensive interchain hydrogen bonding along the glucan chains results in the formation of bundles of microfibrils held together in a highly ordered structure (Gardner and Blackwell 1979). This results in the development of innumerable crystalline regions. The extraordinary mechanical strength of cellulose is dependent upon the spatial arrangement of glucose residues and also glucan chains.

9.1 *Physical and chemical characteristics*

In ATIRA, Ahmedabad, much work has been done on various facets of cellulose chemistry, particularly in relation to its application in textile and paper industries

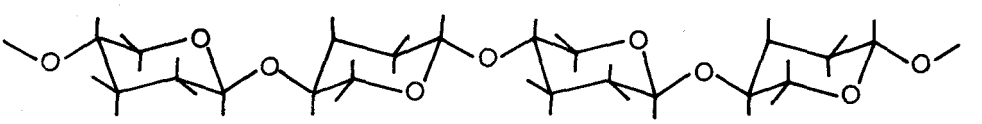


Figure 22. Structure of cellulose.

(Srivastava 1974). In-depth studies have been carried out on the x-ray diffraction measurement of the degree of crystallinity, indicating 72% of crystallinity in raw cotton. As the maturity of the cotton fibers increased, there was enhanced toughness. Thorough investigations have been made on the rupture properties of dry and wet cotton (water absorption results in the removal of strains within the fiber as well as a lubrication effect due to the rupture of some of the existing H-bonds and formation of new H-bonds). The various physical-mechanical-optical characteristics of swollen cotton and mechanics of cross-linked (with formaldehyde) cotton have been studied.

Some aspects of the structure of cotton cellulose have been reviewed. It is suggested that the helical structure proposed for cellulose I as per the morphological and structural studies could be extended to cellulose II and to the examination of other types of helix.

The concentration of cellulose varies with maturity of legume plants (Bailey 1971). In legumes cellulose is normally recovered as the alkali-insoluble residue left after the extraction of alkali-soluble hemicelluloses. On a dry weight basis, 8–10% is present in stems and 5–9% in leaves. The husk of many legumes is invariably rich in cellulose, which constitutes dietary fiber. Legume plant celluloses do not appear to have been examined in any detail.

The presence of minor quantities of other glycoses is sometimes noticed in cellulose hydrolysates (Muehlenthaler 1967). These non-glucosyl residues might be true constituents of glucan molecule, perhaps representing termination points in the chain. Alternatively, the non-glucosyl sugars could originate from the associated, tightly-bound hemicellulosic polysaccharides, obviously because of their close structural similarity (particularly xylans and xyloglucans) with cellulose (Timell 1964, 1965).

The growth of mildew on jute fibers and its consequent damage is a serious problem causing stains, loss in strength, a musty odour and sometimes even bad hygiene. Humidity ($\sim 15\%$) is necessary for the growth of mildew. Detailed studies carried out at IJIRA, Calcutta, have indicated that drying of jute (consequently its cellulose component) below 15% moisture is a prerequisite to prevent fungal attack, suggesting that the action of cellulosic enzymes is restricted by the non-availability of water. It is reported that the role of water under such limiting conditions is to affect the active site of the enzyme protein, which is otherwise conformationally stabilized by water; and secondly its involvement as the reagent for hydrolysis (Kundu *et al* 1982). Water helps in restoring conformation of the active site of the enzyme molecule, rather than the stoichiometric reaction. Moisture above this level ($> 15\%$) helps in hydrolytic reaction, and its rate therefore increases.

9.2 *Cellulose derivatives and their uses*

A considerable amount of work has been done on the morphology, crystalline structure, porosity and thermodynamic behaviour, and response to chemical treatment on the never-dried and nature-dried cotton (Srivastava 1974). The sorption of dyes and chemicals on cellulose has been investigated with particular reference to various aspects of textile dyeing (Srivastava 1974). The present day concept of clothing has changed considerably, a wide variety of improved fibers having advantages like attractive look, smooth feel, easy-to-wash and wear are called for.

Accordingly, cellulose fibers were chemically modified to possess these attributes. Incorporation of halogen atoms in cellulose imparts certain desirable properties like flame retardancy, oil and water repelling and bacteriostatic effects. A variety of reagents such as mesyl chloride in DMF at 65°C for 24 h, thionyl chloride-DMF and other combinations have been utilized for this purpose. Bromodeoxy cellulose, prepared by bromination of 6-0-tosyl cellulose with lithium bromide in DMF at 65°C for 3 h, gave a product having good flame resistance and stability for over 6 months (Srivastava 1974). The fluorodeoxy cellulose, obtained by treatment of tosyl ester of cellulose with potassium fluoride was of interest for imparting oil and water repellency to cotton fabrics (Srivastava 1974).

Introduction of unsaturation between C-5 and C-6 positions of the glucose residues of cellulose offered a convenient starting material for synthesizing a wide variety of cellulose derivatives (Srivastava 1974).

Polymer grafting was another synthetic approach for preparing copolymers (attached by covalent linkages may be as an appendage to the backbone of another polymer) of desirable characteristics, and finding use in textile industries (Srivastava 1974). Acrylic acid and its esters-acrylamide, acrylonitrile, vinyl acetate and styrene are some of the commonly used grafting reagents. The free radicals required for grafting are generated by UV or high energy radiation, by γ-rays or an electron beam or by chemical reactions using redox systems. The acrylonitrile-cellulose grafts have decreased moisture regain, increased tensile strength, dyeability with basic dyes without the use of mordant, and rot resistance (Srivastava 1974).

The various drawbacks such as poor elasticity, abrasion resistance and durability, and increased susceptibility to microbial attack, shrinking properties when wet, and appearance of much crease in cotton (fabrics) on washing, have been overcome by cross-linking (Srivastava 1974). The process actually involves treatment of cotton with an aqueous solution containing a cross-linking agent, a catalyst, an additive (to impart smoothness and softness) and a wetting agent. A variety of cross-linking agents such as urea, thiourea, formamide, formaldehyde, etc, are available in literature. The cross-linked cellulose has reduced toughness, swelling capacity in water, tensile strength, tear strength and abrasion resistance. However, the extent of reduction in these properties depends essentially on the number of cross-links formed, as also on their location and distribution in the fiber structure. An uneven distribution gives a smooth and crease-free appearance.

Chemical modifications, viz oxidation and reduction have been attempted to various extents to improve the reactivity of cellulose towards reactive dyes such as Procion series, Remazol, Primazene, etc (Srivastava 1974). This also helps in increasing the wash fastness of the dyed and printed fabric. By using model carbohydrate compounds and cellulose investigations have been made on the site of reaction of reactive dyes (Srivastava 1974).

From jute stick, an agrowaste left out after the separation of jute fiber, a series of cellulose derivatives, viz carboxymethyl cellulose, microcrystalline cellulose, cellulose acetate, cellulose xanthate, etc have been prepared (Banerjee and Day 1984). These derivatives find extensive application in the manufacture of rayon, cellophane, etc.

A reversed dye-partition technique using Disulphine Blue has been used to determine the degree of substitution of sodium carboxymethylcellulose (Mukhopadhyay *et al* 1973).

A cellulose column chromatographic method has been developed for the quantitative separation of starch components (Patil and Kale 1973). The cellulose column was equilibrated with ethanol-urea and the adsorption of amylose was induced by ethanol, whereas the amylopectin was washed off the column. Amylose was then eluted with a gradient of ethanol-urea, and the recovery was ±95%. Some intrinsic heterogeneity of amylose was, however observed.

9.3 *Biotechnology*

In the biotechnology unit of IIT, Delhi, much work has been done on the total utilization of renewable energy resources such as bagasse, rice straw, cellulose and cellulosic wastes, etc in the form of ethanol and as mixed feed production. The cellulose to ethanol conversion requires a series of operations like delignification, cellulose production, saccharification, conversion of sugars to ethanol, and separation of ethanol. *Trichoderma reesei* was found to be the best known organism for cellulase production (Ghose and Sahai 1979). Developments in the reactor have been made to include built-in continuous recycle system of solid components of the medium to a constant uniform concentration (Anonymous 1984). A mixed culture fermentation employing both cellulase and hemicellulase enzymes was found to be more advantageous in the hydrolysis of native cellulosic residues such as bagasse. Direct conversion of cellulose into ethanol using the anaerobe *Clostridium thermocellum* under vacuum cycling has also been tried (Anonymous 1984).

Studies were also made on the isomerization of glucose to high-fructose syrup by using immobilized *Actinoplanes* cells (containing the isomerase activity of 460 IU/g) (Anonymous 1984). Bioconversion of xylose present in hemicellulosic hydrolyzate using cells of *Trichosporium* has resulted in xylitol (45–55%), another potential sweetner (Anonymous 1984).

A method has been standardized for bioconversion of glucose to gluconic acid by immobilized *Aspergillus* spores on pumice stone (Anonymous 1984).

10. Future needs of carbohydrate research

There exists a conceptual and technological gap in the realization that carbohydrates are vital for our normal existence and also for other forms of life. In spite of the enormous progress in diversified areas of carbohydrate research, our understanding of the structure-function relationships in ragard to various physical properties such as hydration, viscosity, cooking quality and texture of the finished food products, and the medicinal value of some of the natural gums/mucilages and various other plant polysaccharides is rather meagre.

Occasionally polysaccharides are found to be present in covalent association with proteins, either as proteoglycans in which the protein component carries polysaccharide substituents, or as glycoproteins in which the protein is a major component. A particular example is of the varied functional-physiological roles played by arabinogalactan-proteins which are widely distributed in plant tissues, gum exudates, and are also produced by many callus cells in tissue culture (Clarke *et al* 1979). It is suggested that arabinogalactan-proteins are involved in the adhesion of callus cell clumps which respond very well by an increase or decrease in the content of arabinogalactan to alterations in the environment, such as temperature. If so, how

is this subtle function expressed to balance the physiological status of the tissue culture (and of the plants) remains yet to be understood.

The interactions, viz polymer-polymer association and polymer-(small) ligand interactions occurring in nature helps to assist the living organism with specialised biological functions. Many of these interactions are involved in specific recognition phenomena (immunbiology).

The terminal sugar residues of plant gums (and of many biological glycoconjugates) have been shown to be of taxonomic significance (Anderson and Dea 1969). In other words these terminal sugar sequences, although possessing common core structures, may be implicated in the expression of identity of individual plants, tissues and cell types. The ability of plant and animal cell lines to accept or reject foreign grafts implies the existence of a precise mechanism for mutual recognition of the tissues involved. Typical cell surface constituents namely receptors are involved in this recognition and expression of identity. This is an area of intense study now.

There is not much progress in the localization within the tissues of the various macromolecules particularly the glycoconjugates. Although a great deal of information is available on the chemical makeup of a variety of these macromolecules, there is little knowledge regarding their formation (biosynthesis) and localization at the ultrastructural level. This is mainly due to the lack of precise cytochemical methods for their detection. Such knowledge seems a prerequisite to an understanding of their function.

The therapeutic-pharmacological value of dietary fiber components is very well recognised all over. So far it is not clear whether it is a total effect or whether it is due to one fraction of the total carbohydrates and if so whether there is any specificity with respect to the makeup and sequence of its constituent monosaccharides. Is this particular fraction universally present in dietary fiber fractions from various sources? Is there a better, convenient and quick way of estimating-analysing all the dietary fiber components? Whether any specific polysaccharide fraction is capable of expressing the dietary fiber action? All these aspects need clarification.

It is not documented yet whether small amounts of protein, presumably from the cell walls enclosing the starch granules together with insoluble proteins found always associated with legume starch granules are an integral part of the glycan molecule? This is because recently the glycoprotein nature of starch was reported (Tandecarz *et al* 1975). Precise biosynthetic knowledge about the formation of starch granules of different shapes and sizes, the layered internal structures present in many of the starch granules, the role of various non-starch components, viz free and bound lipids, protein, inorganic metal ions, bound water, etc in maintaining the integrity of the granule is not yet available. All these are topics of great academic and technological interest warranting further detailed studies.

There is a tremendous demand by food and non-food industries for the use of native and modified starches and gums or substituents. As an alternative to corn and maize starches which have food value, search for new-indigenous sources of starch (or substituents) is necessary.

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Abbreviations used: Ara, arabinose; Xyl, xylose; Gal, galactose; Glc, glucose; Man, mannose; Fuc, fucose; Rha, rhamnose; GlcA, glucuronic acid; GalA, galacturonic acid; NSP, non-starchy polysaccharide;

DEAE-diethylaminoethyl-; DP, degree of polymerization; DS, degree of substitution; DE, degree of esterification, M_r, molecular weight; BU, Brabender units; PC, paper chromatography; GLC-MS, combined gas liquid chromatography-mass spectrometry; NMR, nuclear (^1H or ^{13}C) magnetic resonance spectroscopy; SEM, scanning electron microscopy; IR, infra red spectroscopy; UV, ultraviolet (radiation); DMSO, dimethyl sulfoxide; DMF, dimethyl formamide; TFA, trifluroacetic acid; TCA, trichloroacetic acid; ND, not determined.

All sugar residues are glycosidically linked at C-1. Thus, D-Manp-β-1,4-D-Manp is a disaccharide in which a D-manno-pyranosyl residue is attached by a β-glycosidic bond from its C-1 to C-4 of a D-mannopyranose residue.