CHAPTER - I

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The polysaccharides have a very wide distribution in nature. Cellulose and chitin are found as the skeletal material of plants and animals, while others, like starch and glycogen, occur as reserve substances, readily convertible as required into energy.

Polysaccharides are high molecular weight carbohydrates, are viewed as condensation polymers in which monosaccharides or their derivatives have been glycosidically joined with the elimination of water.

Some polysaccharides have linear molecules with all the sugar units linked in one unbranched chain, whereas others have branched molecules containing a main chain to which smaller chains are linked glycosidically. Some polysaccharides have a highly branched structure.

The classification of plant polysaccharides is based on their chemical composition and structure[1]. In such a classification the polysaccharides hydrolysing to only a single monosaccharides type would be placed in a group which may be termed as homoglycans, while the polysaccharides with two or more than two types of monosaccharide units would be placed in a separate group termed as heteroglycans. A systematic and broad classification of natural polysaccharides is given in Table 1.1.

Table 1.1

Classification of Natural Polysaccharides

Natural polysaccharides

- **Homoglycans**
  - **Nitrogenous polysaccharide**
    - i) Glucosamine polymer
  - **Neutral polysaccharides**
    - i) Glucans
    - ii) Mannans
    - iii) Galactons
    - iv) Fructans
  - **Acidic polysaccharides**
    - i) Galacturonans
    - ii) Mannuronans
    - iii) Gluronans
- **Hetroglycans**
  - **Nitrogenous polysaccharides**
    - i) Mucopoly-saccharides
    - ii) Glycoproteins
  - **Neutral polysaccharides**
    - i) Hemicellulose
    - ii) Galactomannans
    - iii) Glucomannans
    - iv) Arabinogalactans
    - v) Arabinoxylans
    - vi) Xyloarabinans
  - **Acidic polysaccharides**
    - i) Gums
    - ii) Mucilages

Natural polysaccharides can be further classified by considering their structures either as branched polysaccharides or Linear polysaccharides.

This separation can readily be made by performing several simple tests[2]. The easiest test is that of film formation. In an aqueous test polysaccharide solution when spread on a glass plate and dried will be brittle if a branched polysaccharide is present. Films from linear polysaccharides will be strong, undergoing folding without breaking. Branched polysaccharides are easily soluble in water and have immense thickening power. Cellulose is an example of branched polysaccharide, but it also has partly nature of linear polysaccharides.

By considering the sources of polysaccharides there are three major types of polysaccharides :

a) Phytopolysaccharides

b) Bacterial and Fungal polysaccharides

c) Zoopolysaccharides.

Phytopolysaccharides are obtained from plants. The major examples of phytopolysaccharides are cellulose, starch galactomannan, frutans.

Aspergillus polysaccharides and Leuconostoc polysaccharides are the examples of Fungal and Bacterial polysaccharides.

Polysaccharides obtained from animals are zoopolysaccharides. Many of the zoopolysaccharides exist in the animal and in isolated products as loose salt complex or chemically bonded with proteins. Zoopolysaccharides are further classified as :

a) Zooglycans

b) Protein zoopolysaccharides

c) Zooglycolipids

d) Zooglycolipoproteins.

Some polysaccharides like chitin, cellulose occur in plants as well as in animals.

The polysaccharides in the form of gums and mucilages are often used in curing ringworm, bacillary dysentry, arithritis, infantile diarrhoea, enlargement of liver and chronic cough etc. Recently the polysaccharides[3] extracted from natural sources have been reported to possess high drug potentiality against cancerous and tumorous growths. The degree of antitumor action of these polysaccharides was observed to be dependent upon the nature and mode of glycosidic linkages present in the molecular structure of polymer concerned. The polysaccharides[4] also play the role of an antibiotic during covering and filling of bone defects at the time of insertion of dental implants.

The polysaccharides especially galactomannans are substances of industrial importance. The galactomannans[5] isolated from the seed mucilage of the family, Leguminoseae are used as thickening and gelling agents in food industry, as binding agents in pharmaceutical industry, as clarifying agents in sugarcane industry, as sizing material for textiles in textile industry, and as additives in insecticidal and herbicidal compositions. Natural gums[6] containing galactomannose (0.01 - 10 parts) as main component when added to 100 parts of $CaSO_4 \cdot 5H_2O$, plasters improve its water retention properties and prevents hardening defects such as cracking.

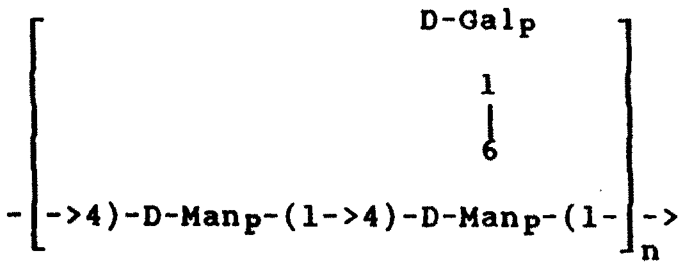
The polysaccharides have large number of medicinal and industrial applications, therefore, the structure of the polysaccharides is always a subject matter of interest to organic chemist. Investigation of structure of plant polysaccharides is useful to study the mechanism by which simple sugars are transformed into other hexoses, pentoses, uronic acids and methyl pentoses. The recent use of polysaccharides in cancer chemotherapy has stimulated further the interest of organic chemists to understand the structure activity relationship of these compounds.

In recent years, the phytochemists are studying the gums occuring in plant seeds. Seed gums are considered superior to plant gums. A systematic study of the plant polysaccharides is continuing for more than 40 years in various research laboratories of India. Table 1.1 shows some plant sources from which the polysaccharides have been isolated for the purpose of their structural studies.

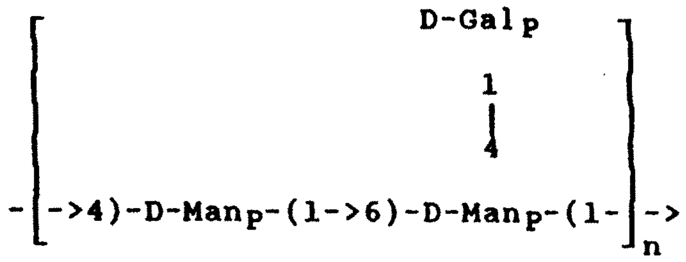
A literature survey shows that a large number of the plants belonging to Leguminoseae family have been chemically screened so far. Anderson[74] has examined 163 Leguminoseae plants while Faroogi et.al.[75] have reported the screening of seeds of 237 Leguminoseae plants. Both the investigators have shown that the plants belonging to Leguminoseae family produce seeds rich in mucilageneous matter. The survey of literature also shows that the polysaccharides occuring in the seeds of the plants of Leguminoseae family are a generally galactomannan type. Galactomanns are the common water soluble constituent of endosperm and are considered as reserve polysaccharides. Galactomannans are the polysaccharides which produce only galactose and mannose after complete hydrolysis. Appreciable volume of literature has accumulated on the structure of galactomannans during the past few years.

The galactomannan[28] from the seeds of Sesbania grandiflora has been reported to be a neutral polysaccharide containing two major sugars i.e.D-galactose and D-mannose in molar ratio of 1:2. The hydrolysis of the fully methylated compound furnished 2,3,4,6 - tetra-o-methyl D-galactose, 2,3,6 - tri-o-methyl D-mannose and 2,3 di-o-methyl D-mannose in a molar proportion 1:1:1. Upon periodate oxidation, the polysaccharide consumed 1.2 moles of periodic with simultaneous liberation of 0.34 mole of formic acid per mole of anhydrohexose unit. On Smith's degradation of periodate - oxidised material, it furnished glycerol and erythritol in a molar ratio 1:1:8.

Based on the results of methylation and periodate oxidation and Smith degradation studies, Shrivastav and his co-workers have proposed four possible structures shown below, for the galactomannan, none of which could be confirmed. Therefore, it was decided to study graded hydrolysis of the seed polysaccharides obtained from Sesbania grandiflora. It was further also decided to study Proton NMR and C^{13} NMR study of the polysaccharide.



(1)



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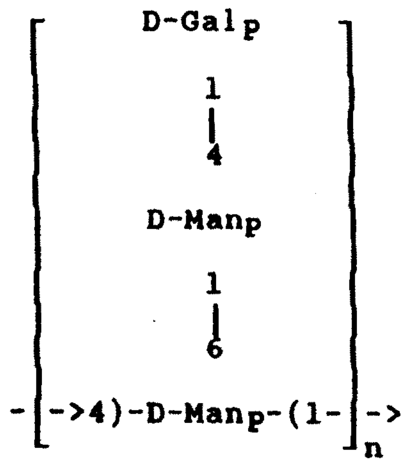

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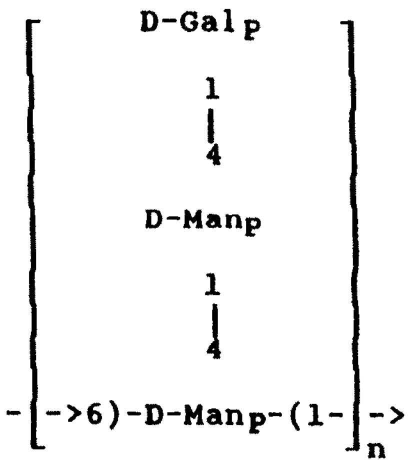

(4)

TABLE 1.1

A List of Plant Material Investigated at Research Laboratories of India

Sr. No.	Name of the Plant	Natural order	Nature of the polysaccharide	References
1.	Azadurachta indica	Meliaceae	Gum	7- 8
2.	Odina wodeir	Anacardiaceae	Gum	9-11
3.	Acacia sundra	Leguminoseae	Gum	12-13
4.	Salvia aegyptiaca	Labiatae	Mucilage	14
5.	Feronia elephantum	Rutaceae	Gum	15
6.	Saccharum officinarum	Gramineae	Hemicellulose	16-17
7.	Chloroxylan swietenia	Rutaceae	Gum	18
8.	Commiphora mukul	Burseraceae	Gum	19-20
9.	Salmalia malabarica	Bombacaceae	Gum	21
10.	Anacardium occidentale	Anacardiaceae	Gum	22-23
11.	Hibiscus ficulneus	Malvaceae	Mucilage	24
12.	Anacardium occidentale shell	Anacardiaceae	Shell poly saccharide	25-27
13.	Sesbania grandiflora	Leguminoseae	Seed poly-saccharide	28
14.	Cassia absus	Leguminoseae	Seed poly-saccharide	29-32
15.	Phoeni dactyliferara	Palmae	Seed poly-saccharide	33-34
16.	Cassia fistula	Leguminoseae	Seed poly-saccharide	35-36
17.	Cassia occidentalis	Leguminoseae	Seed poly-saccharide	37-38

Sr. No.	Name of the Plant	Natural order	Nature of the polysaccharide	References
18.	Ocimum basilicum	Labiataeseae	Seed polysaccharide	39-40
19.	Aegle marmelos	Rutaceae	Gum	41-42
20.	Cassia grandis	Leguminoseae	Seed polysaccharide	43-44
21.	Crotalaria juncea	Leguminoseae	Seed polysaccharide	45-46
22.	Cassia multijuga	Leguminoseae	Seed polysaccharide	47
23.	Strychnos potatorum	Loganiaceae	Seed polysaccharide	48
24.	Aloe vera	Liliaceae	Mucilage	49
25.	Ipomoea fistulosa syn.I. carnea	Convolvulaceae	Seed polysaccharide	50
26.	Woodfordia fruiticosa	Lythraceae	Gum	51
27.	Sesbania speciosa	Leguminoseae	Seed polysaccharide	52
28.	Sesbania aegyptiaca	Leguminoseae	Seed polysaccharide	53
29.	Cassia corymbosa	Leguminoseae	Seed polysaccharide	54
30.	Cassia renigera	Leguminoseae	Seed polysaccharide	55-56
31.	Cassia laevigata	Leguminoseae	Seed polysaccharide	57
32.	Teramnus labialisora	Leguminoseae	Seed polysaccharide	58
33.	Melilotus indica	Leguminoseae	Seed polysaccharide	59

Sr. No.	Name of the Plant	Natural order	Nature of the polysaccharide	References
34.	Indigofera tintoria	Leguminoseae	Seed polysaccharide	60
35.	Cassia sophera	Leguminoseae	Seed polysaccharide	61
36.	Acacia leucophloea	Leguminoseae	Seed polysaccharide	62
37.	Linum usitatissimum	Linaceae	Seed polysaccharide	63
38.	Cassia alata	Leguminoseae	Seed polysaccharide	64-65
39.	Melilotus officinalis	Leguminoseae	Seed polysaccharide	66
40.	Crotalaria verrucosa	Leguminoseae	Seed polysaccharide	67
41.	Cassia siamea	Leguminoseae	Seed polysaccharide	68
42.	Sesbania bispinosa	Leguminoseae	Seed polysaccharide	59
43.	Ipomoea palmta	Leguminoseae	Seed polysaccharide	70
44.	Cassia ovata	Leguminoseae	Seed polysaccharide	71
45.	Cassia surattensis	Leguminoseae	Seed polysaccharide	72
46.	Prosopis cineraria	Leguminoseae	Seed polysaccharide	73