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GLUCANS OF HIGHER PLANTS

A. O. Arifkhodzhaev

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This review gives literature information on the glucan polysaccharides of higher plants, excluding glucans of the type of starch and cellulose.

Polysaccharides are biopolymers of high molecular weight that have been known from comparatively ancient times and are widely used in folk medicine. The bulk of the dry mass of higher plants is due to polysaccharides, the functions of which are exceptionally diverse. The main polysaccharide components of the plant cell wall are cellulose, hemicelluloses, and pectin substances. Starch, glucofructans, glucomannans, galactans, glucans, etc., are among the main reserve substances [1, 2].

The most studied among the polysaccharides are the glucans, which have been isolated from bacteria, fungi, animals, algae, higher and lower plants, and other sources, and differ from one another in properties and structures.

Plant polysaccharides are extremely diverse and fulfil various biological functions, depending on the species and their localization in the plants. Glucans have been isolated from the epigeal and hypogeal organs of higher plants. Their characteristics are given in Table 1.

As can be seen from Table 1, the molecular masses of these polysaccharides range from 4200 in sorghum grain [33] to $1 \cdot 10^6$ c.u. in *Mangifera indica* L. [26, 27]. The molecular mass substantially affects the physical properties of the glucans. Glucans of low molecular mass dissolve readily in cold water, but with increasing degree of polymerization the rate of their dissolution falls and viscous colloidal solutions are formed, although in some cases this tendency in solubility is not observed.

Isolation and Purification

In the majority of cases, for the isolation of polysaccharides the plant material is first extracted with hot methanol or ethanol in order to eliminate pigments, low-molecular-mass compounds, and substances of noncarbohydrate nature. In view of the fact that a number of glycans are readily soluble in water, water is used for their extraction. Extraction is performed most frequently with aqueous solutions of sodium hydroxide [10, 18, 19] or of lead hydroxide [9] [sic] or with aqueous methanol [30] or aqueous ethanol [20]. The elimination of accompanying compounds is achieved by methods described in the literature [37-40].

The purification of the glucans is carried out by fractional precipitation with alcohol, which permits the preparative separation of large amounts and the enrichment of individual fractions [41].

To determine the homogeneity of the fractions in terms of molecular mass, use is made of electrophoresis [42], ultracentrifugation [43], and gel filtration through Bio-Gels and Sephadexes of various types [44]. Ultracentrifugation and gel filtration provide the possibility of establishing molecular masses and achieving a preparative separation of the glucans.

Methods of Investigation

Modern methods of establishing the structures of polysaccharides are applied only to individual substances, since work with unpurified polysaccharides may lead to far from true results. A polysaccharide is usually considered to be an individual

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 40 64 75. Translated from Khimiya Prirodnykh Soedinenii, Vol. 33, No. 1, pp. 3-15, January-February, 1997. Original article submitted June 27, 1994.

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TABLE 1. Characteristics of the Glucans of Higher Plants

Plant species (family), organ	Name of the polysaccharide	Mol. mass, c.u.	$[\alpha]_D$, deg.	Type of bonds	Literature
1. Acanthopanax senticosue (Araliaceae), roots	As-11	150000	+167	α-(1→6),(1→2)	3
2. Acanitum carmichaeli (Ranunculaceae), roots	Aconitan-A	8700	+190	α-(1→6),(1→3)	4
3. Aloe arborescens (Liliaceae), leaves	Polysaccharide-A	15000	+95	α-(1→6)	5
4. Althaea officinalis (Malvaceae), leaves	Glucan	–	–	α-(1→6)	6
roots	D-Glucan III	–	–	α-(1→6)	7
5. Angelica acutiloba (Umbelliferaceae), roots	AR-Glucan	135000	–	α-(1→4),(1→6)	8
6. Arundinaria japonica (Bambuseae), leaves stems	Glucan-P_1	–	-6.2	β-(1→3),(1→4)	9
7. Astragalus mongholicus (Leguminosae), roots	Glucan	50000	–	β-(1→4),(1→6)	10
8. Avena sativa (var. Blenda) (Aveneae), leaves	Glucan	–	-5.2	β-(1→3),(1→4)	11–15
9. Biebersteinia multifida DC. (Biebersteiniaceae), tuberous roots	Glucan-A	4100	+150	α-(1→6),(1→3)	16
	B	2200	+130	α-(1→6),(1→3)	17
	C	1100	+110	α-(1→6),(1→3)	
10 Cinnamomum zeylanicum (Lauraceae), bark of the stems	Glucan	200000	+99	α-(1→4),(1→6)	18
11 Hordeum distichum L.var.Betzes (Hordeeae), endosperm	β-*D*-Glucan	180000	–	(1→3),(1→4)	19
12. H.bareale Scribn. et Smith, endosperm	F-1-β-Glucan	220000	–	β-(1→3),(1→4)	20–22
	F-4-β-Glucan	–	–	β-(1→3),(1→4)	23
13. H.vulgare, endosperm	Polysaccharide	–	–	β-(1→4),(1→3)	24

TABLE 1 (continued)

Plant species (family), organ	Name of the polysaccharide	Mol. mass, c.u.	$[\alpha]_D$, deg.	Type of bonds	Literature
14. H.julia H.zephyr H.Golden promise	β-*D*-Glucan	-	-	β-(1→4),(1→3)	25
15. Mangifera indica L. (Anacardiaceae), fruit	Glucan	10000000	+165.8	α-(1→3),(1→4)	26, 27
16. Mirobilis jalapa (Nyctaginaceae), bulbs	Polysaccharide	-	+33	(1→3),(1→4)	28
17. Oryza sativa L. (Oryzaae), bran	RDP	-	-	α-(1→6),(1→4)	29
18. Panax ginseng (Araliaceae), roots	Panaxan- A	14000	+187	α-(1→6),(1→3)	30, 31
	B	-	+180	-	
	C	-	+96	-	
	D	-	+126	-	
	E	-	+188	-	
19. Sawa millet (Paniceae), endosperm	α-*D*- Glucan	11000	-	α-(1→4),(1→6)	32
20. Sorghum grain (Andropogoneae), endosperm	β-*D*- Glucan	4200	-	β-(1→3,(1→4)	33
21. Zea mays L. (Gramineae),					
stems	Glucan	20570	-5	β-(1→3),(1→4)	34
shoots	Glucan	70000	-	β-(1→3),(1→4)	35
galls	Glucan	-	-40	β-(1→3),(1→6)	36

TABLE 2. Mass-Spectrometric Fragments of Partially Methylated Acetates of Polyols Derived from Glucose

Acetates of the polyols	Time, min	m/z	Bond	Literature
2,3,4,6-Tetra-O-Me-Glc*	1.0	43, 45, 71, 87, 101, 117, 129, 145, 161, 205	Glc-(1→	8, 31
2,3,6-Tri-O-Me-Glc	2.3	43, 45, 87, 99, 101, 113, 117, 233	→4-Glc-(1→	8
2,3,4-Tri-O-Me-Glc	2.05	43, 87, 99, 101, 117, 129, 161, 189	→6)-Glc-(1→	31
2,3-Di-O-Me-Glc	4.5	43, 101, 117, 261	→4)-Glc-(1→ 6 ↑	8
2,4-Di-O-Me-Glc	3.60	43, 87, 117, 129, 189	→6)-Glc-(1→ 3 ↑	31

*"2,3,4,6-Tetra-O-Me-Glc" represents 1,5-di-O-Ac-2,3,4,6-tetra-O-Me-*D*-sorbitol.

substance if on fractionation by several methods its monosaccharide composition and its physicochemical characteristics (specific rotation, molecular mass, etc.) do not change and generally adopted analytical methods confirm the absence of impurities.

To establish the structure of a glucan it is necessary to determine its molecular mass, its qualitative and quantitative monosaccharide compositions, the configurations of its glycosidic bonds, the presence and positions of branch-points, and the size of the oxide rings, and to establish the type of bonds between the individual monosaccharides and the positions of noncarbohydrate components. To solve these problems, the chemical methods employed in establishing the structures of all types of polysaccharides, including glucans, are used. Such methods are methylation, periodate and chromic oxidation, reduction, acetolysis, etc. In the case of glucans, additionally, the structures of the oligosaccharides produced by their partial acid hydrolysis and enzymatic hydrolysis are studied. These methods have been described in detail in the literature, and we shall therefore give only a few examples of their use for establishing the structures of glucans.

The roots of *Aconitum carmichaeli* have yielded a glucan with a molecular mass of 8700, $[\alpha]_D$ +190°, which has been called aconitan-A [4]. In a hydrolysate of the glucan, only glucose was detected by paper chromatography (PC) and gas-liquid chromatography (GLC). The homogeneity and molecular mass of the glucan were determined by gel chromatography on Sephadex G-75.

The size of the oxide rings, the presence of branching, and the type of bond were determined by the Smith degradation of the polysaccharide: the degradation products were found to contain glycerol and 5.8% of free glucose [45]. The formation of glycerol showed the presence of 1→6-bonds between monosaccharide residues, while the detection of free glucose indicated the possibility of branching in the glucan chain at the C-3 atom of glucose.

Aconitan-A was subjected to acetolysis, and nigerose was detected among the products; consequently, the glucan also includes 1→3 bonds between monosaccharide residues.

The polysaccharide was then methylated by Hakomori's method [46]. By TLC and GLC the hydrolysis products of the permethylate were found to include 2,3,4,6-tetra-O-Me-*D*-glucose, 2,3,4-tri-O-Me-*D*-glucose, and 2,4-di-O-Me-*D*-glucose in a ratio of 1.2:9.0:1.0, respectively. The presence of 2,3,4,6-tetra-O-Me-*D*-glucose showed that the nonreducing end was glucose, while the detection of 2,3,4-tri-O-Me-*D*-glucose showed 1→6-bonds between the hexose residues. The presence of 2,4-di-O-Me-*D*-glucose confirmed the results of periodate oxidation and acetolysis.

On the basis of the results obtained, the authors came to the conclusion that the glucan under study from *Aconitum carmichaeli* was an α-1→6-bound glucan having branches at C-3 atoms of glucose residues.

A glucan called panaxan-A, isolated from ginseng roots, has a molecular mass of 14,000, $[\alpha]_D$ +187° [31]. The methods described above were used in the study of the structure of this polysaccharide. It was established from the results of methylation, periodate oxidation, and spectral methods that the glucan had a main chain consisting of α-(1→6)-bound glucopyranose residues to which, in the C-3 positions, were attached side-chains of α-(1→6)-bound glucopyranose residues: the ratio of terminal, 6-substituted, and 6,3-disubstituted *D*-glucopyranose residues was 1.0:2.0:1.0.

According to the results of gel chromatography and electrophoresis, glucans A, B, and C, isolated from *Biebersteinia multifida* [17], were homogeneous. The molecular masses of glucans A, B, and C were determined by gel chromatography on Sephadex G-50 and by high-pressure exclusion liquid chromatography with calibration by known dextran standards.

TABLE 3. Analysis of the Results of the PMR Spectroscopy of Some Glucans

Name of the polysaccharide	Anomeric proton at δ (d, J = 3 Hz)		Literature
AR-Glucan	4.91	5.30	8
Aconitan-A	4.98	–	4
PS-1	–	5.04	5
Panaxan-A	4.89	5.20	30
B	4.88	5.24	30
C	4.88	5.18	30
D	4.92	5.23	30
E	4.87	5.22	30

The products of the periodate oxidation of glucans A, B, and C after Smith degradation were found to contain glycerol and free glucose. Consequently, the main chains of the glucans consisted of α-(1→6)-bound glucopyranose residues and had branching at glucose C-3 atoms. The results of periodate oxidation were confirmed by the Hakomori methylation of glucans A, B, and C: the hydrolysis products of the permethylates contained 2,3,4,6-tetra-O-Me-*D*-glucose, 2,3,4-tri-O-Me-*D*-glucose, and 2,4-di-O-Me-*D*-glucose in the appropriate ratios for each glucan [17]. The detection of free glucose residues in the products of the chromic oxidation of glucans A, B, and C showed that the glucans were not oxidized because of the presence of α-glycosidic bonds between the glucopyranose residues.

Extraction of the bark of the stems of *Cinnamomum zeylanicum* with alkali followed by gel chromatography on Sephadex G-200 yielded a glucan with a molecular mass of 200,000, $[\alpha]_D$ +99° [18]. The polysaccharide was methylated by Hakomori's method, and the completeness of methylation was monitored by IR spectroscopy. With the aid of GLC and chromato-mass spectrometry, 2,3,4,6-tetra-O-Me-*D*-glucose, 2,3,6-tri-O-Me-*D*-glucose, and 2,3-di-O-Me-*D*-glucose were detected in the methylation products in a ratio of 1.0:43.2:11.0.

Periodate oxidation was conducted at 4°C for 48 h, the consumption of periodate being 1.1 mole per hexose residue. Not only erythritol but also glycerol and glucose were detected in the oxidation products. Analysis of the chromic oxidation products showed that, in the glucan, 85% of the glucose was not oxidized because of the presence of α-glycosidic bonds. Enzymatic hydrolysis of the glucan with the aid of glucoamylase led to the complete hydrolysis of the polysaccharide to *D*-glucose, which showed the presence of α-(1→4)- and α-(1→6)-glycosidic bonds in the polysaccharide under investigation.

Thus, it was established that the main chain of the *C. zeylanicum* glucan was constructed of α-(1→4)-bound glucopyranose residues and of oligosaccharide side-chain fragments also consisting of α-(1→4)-bound glucopyranose residues, attached to the main chain in the O-6 position.

The above-mentioned chemical methods have also been used to establish the structures of other glucans [3, 6-10, 17, 20, 23, 24, 26-28, 32-35].

Together with chemical methods, spectral methods of investigation, such as IR, PMR, ^{13}C NMR spectroscopy, and mass and chromato-mass spectrometries are widely used. These methods confirm the results of the chemical methods of investigation, and sometimes provide complete information on the structures of oligo- and polysaccharides. Below, we give some examples of the use of spectral methods for establishing the structures of glucans.

Pyranose, furanose, and acyclic forms, the natures and position of functional groups, the molecular masses of the mono- and oligosaccharide residues, and the positions of the glycosidic bonds in oligosaccharides are determined with the aid of mass spectrometry. Because of the low volatility of mono- and oligosaccharides, they are converted into suitable volatile derivatives. The mass spectra of acyclic forms of the monosaccharides in the shape of trifluoroacetates, trimethylsilyl ethers, and acetates of methyl ethers are susceptible of the easiest interpretation [8, 31] (Table 2).

^1H NMR spectroscopy is used in a number of cases to compare different polysaccharides and also for studying glucose-containing oligo- and polysaccharides. With sufficiently good resolution and a reliably identified PMR spectrum of a polysaccharide, the sequence of monosaccharide residues can be determined from the nuclear Overhauser effects (NOEs) arising on the successive preirradiation of the anomeric protons: such preirradiation causes an enhancement or weakening of the signals not only of spatially close protons in the corresponding residue but also of the signals of protons in a neighboring, glycosylated, residue. Types of substitution in the residues are revealed by the same procedure, since an appreciable NOE is observed only for protons present in the immediate vicinity of the carbon atom of a glycosylated residue participating in the formation of the glycosidic bond.

Table 3 gives the results of the PMR spectroscopy of some glucans.

^{13}C NMR spectroscopy is one of the most important methods of investigating the structures of polysaccharides and other biopolymers. This method permits the structure of a polysaccharide to be judged and further routes of chemical investigation to be planned.

With the aid of ^{13}C NMR spectra it is possible to determine the configurations of glycosidic bonds, the monomeric compositions of oligo- and polysaccharides, the presence and positions of various substituting groups, and also number-average molecular masses. Substantial differences in the spectra of monosaccharides in the pyranose and furanose forms readily permit the determination of the oxide ring sizes of monosaccharide residues in polysaccharides. In individual cases, ^{13}C NMR spectroscopy makes it possible to do without laborious chemical operations, which is particularly important in the study of a large series of monotypical polysaccharides. In this case, it is sufficient to investigate the structure of one model polysaccharide and to establish the structures of the others by comparing their spectra.

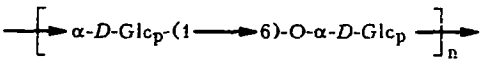
Bradbury and Jenkins have investigated the structures of various trisaccharides by ^{13}C NMR spectroscopy. In their review [47] they give the chemical shifts of monosaccharides and oligosaccharides and their methyl derivatives. Analysis of these results shows that empirical configurational rules can be applied to the interpretation of the structures of trisaccharides with known monosaccharide compositions, and this has been demonstrated on several examples.

In recent years, ^{13}C NMR spectroscopy has been used in almost all studies of the structures of mono-, oligo-, and polysaccharides.

Table 4 gives the chemical shifts of a number of glucans and model compounds. As can be seen from Table 4, by comparing individual chemical shifts of the carbohydrate residues of mono-, oligo-, and polysaccharides it is possible to determine configurations of glycosidic anomeric carbon atoms, linearity, and the positions of substitution and of the glycosidic bonds in the sugar under investigation, etc.

Structures of the Glucans

All the glucans that have been studied have a linear or a branched structure. Linear glucans have been found in plants of the genera *Aloe* [5], *Althaea* [6, 7], *Avena* [11-15], *Hordeum* [22, 24], *Mirabilis* [28], *Oryza* [29], *Sorghum* [33], and *Zea* [35, 36]. The glucans from *Aloe* and *Althea* consist solely of α-(1→6)-bound glucopyranose residues:



(1)

A high-molecular-mass glucan consisting of β-(1→3)- and β-(1→4)-bound *D*-glucopyranose residues in a ratio of 1.0:1.65 has been obtained from the total hemicelluloses of oat leaves [11]. The oligosaccharides obtained on hydrolysis have two types of bonds: β-(1→3) and β-(1→4).

Barley glucans [22] are constructed of β-glucopyranose residues linked by β-(1→4)- and β-(1→3)-bonds in a ratio of 2.5-3.0:1.0. In the glucans the β-(1→3)-bonds are distributed fairly uniformly, alternating with two or three sequences of β-(1→4)-bonds; at the same time a disordered state of these bonds is not excluded. In another barley species [24],. the polysaccharides are constructed of cellotriose and cellotetraose units separated by single β-(1→3)-bonds, although chains containing up to 11 β-(1→4)-linked units are present in smaller amounts. According to the results of Smith degradation, there are no sequences of β-(1→3)-bound residues in the polymers. It has been reported that inclusions of β-(1→3)-bonds impart to the glucan molecules a hydrophilicity and flexibility causing them to dissolve in water.

The glucan of *Mirabilis jalapa* [28] is a linear polysaccharide in which (1→3)- and (1→4)-bound and terminal glucose residues are present in a ratio of 26:8:1. As a result of partial hydrolysis, oligosaccharides containing 2-7 glucose residues have been isolated and characterized:

Glc-(1→3)-Glc, Glc-(1→4)-Glc-(1→3)-Glc
Glc-[(1→3)-Glc]$_2$-(1→3)-Glc, Glc-[(1→3)-Glc]$_5$-(1→4)-Glc

The glucans of maize stems [34] have β-(1→3)- and β-(1→4)-bound *D*-glucopyranose residues in a molar ratio of 1:2. The products of partial hydrolysis include glucose, cellobiose, cellotriose, cellotetraose, laminaribiose, 4-O-β-laminaribiosyl-*D*-

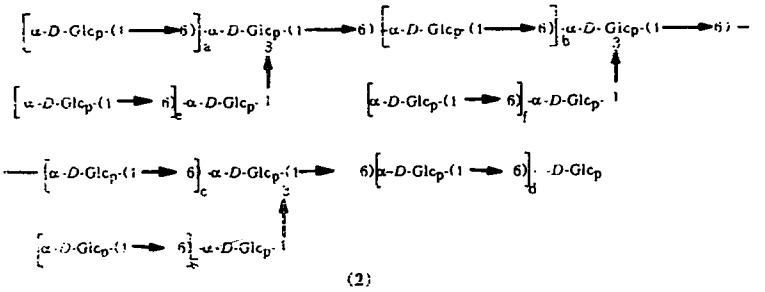
TABLE 4. Chemical Shifts in the ^{13}C NMR Spectra of Glucans and Model Compounds, ppm

Name of the sugar	C-1	C-2	C-3	C-4	C-5	C-6	Literature
Panaxan-A	97.9	71.9	73.3	69.7	70.6	60.6	31
	99.9		81.2			65.6	
AR-Glucan	102.8	74.5	76.4	80.0	74.2	63.5	8
Polysaccharide-A	100.4	74.2	76.2	72.3	72.9	68.2	5
Aconitan-A	100.4	74.1	76.1	72.2	72.9	63.2	4
						68.3	
Glucan-A	98.95	72.65	74.65	70.95	71.45	61.85	48
	99.80		82.50			67.00	
Glucan-B	99.00	72.70	74.65	70.95	71.30	61.85	48
	99.80		82.50			67.00	
Glucan-C	99.00	72.70	74.65	71.00	71.50	61.90	48
	99.80		82.50			67.15	
Maltose	101.0	74.3	74.6	78.5	71.6	62.5	8
Isomaltose	99.4	73.3	75.0	71.3	71.3	67.4	8
Amylopectin	103.2	74.2	76.2	80.9	74.2	63.3	8
Methyl α-glucopyranoside	102.2	74.5	76.0	72.5	74.1	63.5	8

glucose, and 3-O-cellobiosyl-*D*-glucose. The glucans of maize shoots [35] have been treated with various enzymes, and the study of the structures of the oligosaccharides isolated has shown that the initial polysaccharides mainly contained cellotriose and cellotetraose residues linked by β-(1→3)-bonds. In addition, di-, tri- and tetraglucopyranose fragments with 1→3-bonds and blocks containing more than four glucose residues linked by 1→4-bonds, and also fragments with alternating 1→3- and 1→4-bonds, have been detected in these polysaccharides.

Of the branched glucans we must mention the polysaccharides of *Acanthopanax senticosus* [3], *Aconitum carmichaeli* [4], *Angelica acutiloba* [8], *Astragalus mongholicus* [10], *Biebersteinia multifida* [17], *Cinnamomum zeylanicum* [18], *Mangifera indica* [26, 27], and *Panax ginseng* [31].

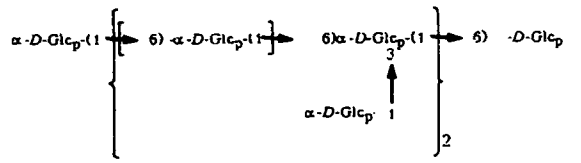
In branched glucans, the points of branching are free glucose hydroxyls. For example, the glucan aconitan-A from *Aconitum carmichaeli* [4] consists of 54 glucopyranose residues:



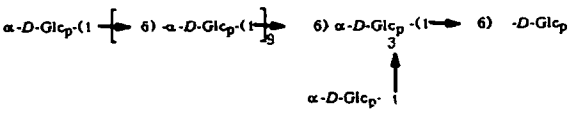
(2)

The main chain of aconitan-A consists of α-(1→6)-bound glucopyranose residues, and branching occurs at the C-3 atoms of glucopyranose units, where α-(1→6)-bound glucopyranose residues are attached to the main chain at three points.

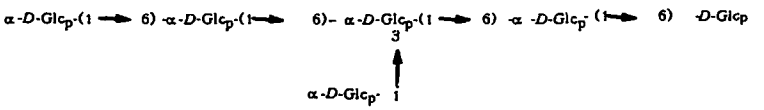
Glucans A, B, and C, isolated from the tuberous roots of *Biebersteinia multifida* [17], are sparingly branched in comparison with aconitan-A and have single glucopyranose residues in the side chains:



Glucan-A (3)

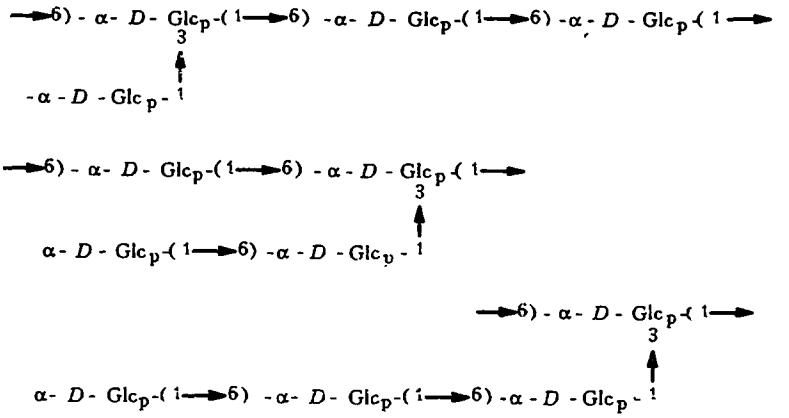


Glucan-B (4)



Glucan-C (5)

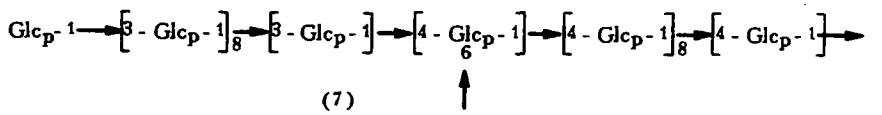
From the roots of *Panax ginseng*, Kanno et al. [30] isolated five biologically active glucans: A, B, C, D, and E. Tomoda et al. [31] established that panaxan-A has a main chain of (1→6)-linked α-glucopyranose residues with a ratio of terminal, 6-substituted, and 6,3-disubstitutes α-glucopyranose residues of 1:1:2. The authors put forward three possible structures of the fragment for panaxan-A:



(6)

A glucan isolated from *Astragalus mongholicus* [10] consisted of a branched structure with a main chain composed of glucopyranose residues linked by α-(1→4)-bonds and had one C-6 glycosidic bond to each nine residues of the main chain.

A glucan has been isolated from ripe mangoes that has the following structure of the repeating unit:



(7)

Sarathy and Gowda [18] isolated a glucan from the bark of the stems of *Cinnamomum zeylanicum* and established that the main chain of the glucan was constructed of α-(1→4)-bound glucose residues; oligosaccharide side-chains also consisting of α-(1→4)-bound glucose residues were attached to the main chain through the C-6 atoms of glucose units. An analogous structure has been established for a glucan isolated from *Angelica acutiloba* [8].

Igarashi [23] established that F-4 β-glucan, isolated from barley endosperm, is sparingly branched, differing thereby from the linear β-glucan F-1 from the same plant: the glucopyranose residues in the molecule are linked by β-1→4 and β-1→3-bonds in a ratio of approximately 2:1.

Thus, the glucans of higher plants have both linear and branched structures, the branch-points in the branched glucans are mainly C-3 and C-6 atoms of the glucopyranose units, and the side-chains may consist of one or more glucopyranose residues.

Biological Activity of the Glucans

Polysaccharides of plant origin are widely used in various branches of the national economy, including medicine. They possess antiinflammatory, antitumoral, antisclerotic, and anticoagulant properties, and also antibiotic activity, and they influence various viral infections, and act on ulcerous diseases of the stomach and the duodenum. There is information about the influence

of various plant polysaccharides on the activitities of some enzymes *in vitro* and *in vivo*. They can be used as blood substitutes, have an antidote activity, etc. [49, 50].

The glucans of higher plants, together with other plant polysaccharides, also possess biological activity. For example, panaxans A, B, C, D, and E — glucans from ginseng roots — possess a hypoglycemic activity [30].

The glucan from the roots of *Acanthopanax senticosus* is an immunologically active polysaccharide, enhancing phagocytosis in immunological tests [3]. An immunological effect has also been revealed in glucan isolated from the roots of *Astragalus mongholicus* [51].

Japanese scientists have patented a glucan from rice bran as an antitumoral immunomodulating agent and an effective component in antiinfection drugs [29].

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