89. M. S. Akutin and L. A. Rodivilova, "Materialy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii, SSSR, Moskva" (Proceedings of the International Symposium on Macromolecular Chemistry, Moscow, USSR), 1960, Section 1, p. 228.
90. V. V. Korshak, T. M. Frunze, and L. V. Kozlov, Vysokomol. Soed., 2, 838 (1960).
91. V. V. Korshak, T. M. Frunze, and V. V. Kurashev, Vysokomol. Soed., 2, 633 (1960).
92. O. Ya. Fedotova, M. L. Kerber, and I. P. Losev, Vysokomol. Soed., 2, 1020 (1960).
93. O. Ya. Fedotova, I. P. Losev, M. L. Kerber, and O. G. Fortunatov, Zhur. Vses. Khim. Obshch. Mendeleeva, 5, 111 (1960).
94. C. W. Stephens, J. Polymer Sci., 40, 359 (1959).
95. W. D. Jones and S. B. McFarlane, U. S. P. 2 667 468 (1954); Chem. Abs., 48, 5553 (1954).
96. R. Hill (Editor), "Fibres from Synthetic Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1957, p. 172.
97. G. J. Berchet, U. S. P. 2 321 890 (1943); Chem. Abs., 37, 6772 (1943).
98. S. Murahashi and T. Takizawa, J. Soc. Chem. Ind. Japan, 47, 784 (1944); Chem. Abs., 43, 4856 (1949).
99. M. Raghavan, B. H. Iyer, and P. C. Guha, J. Indian Inst. Sci., 34, 87 (1952); Chem. Abs., 47, 6889 (1953).
100. O. Bayer, H. Rinke, W. Siefken, and L. Orther, German P. 728 981; Chem. Abs., 38, 381 (1944).
101. J. A. Semers, Brit. Rayon Silk J., 29, 48 (1953).
102. L. Orther, Pat. Application 1.68699 (1941); French P. 892 361.
103. Celanese Corp. of America, B. P. 683 504 (1952); Chem. Abs., 47, 5169 (1953).
104. Celanese Corp. of America, B. P. 685 729 (1953); Chem. Abs., 47, 7257 (1953).
105. Celanese Corp. of America, B. P. 743 918 (1956); Chem. Abs., 50, 12 548 (1956).
106. W. D. Jones and S. B. McFarlane, U. S. P. 2 660 574 (1953); Chem. Abs., 48, 9751 (1954).
107. W. D. Jones and S. B. McFarlane, U. S. P. 2 660 575 (1953); Chem. Abs., 48, 4255 (1954).
108. J. Swerdloff and S. B. McFarlane, U. S. P. 2 658 886 (1953); Chem. Abs., 48, 4253 (1954).
109. E. L. Wittbecker, U. S. P. 2 731 445 (1956); Chem. Abs., 50, 11 054 (1956).
110. E. L. Wittbecker, U. S. P. 2 731 446 (1956); Chem. Abs., 50, 11 054 (1956).
111. A. L. Miller and M. J. Roselle, U. S. P. 2 800 464 (1957); Chem. Abs., 51, 14 320 (1957).
112. E. L. Wittbecker amd M. Katz, J. Polymer Sci., 40, 367 (1959).
113. L. Aleksandru and L. Daskalu, "Materialy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii, 1960, SSSR, Moskva" (Proceedings of the International Symposium on Macromolecular Chemistry, 1960, Moscow, USSR), 1960, Section 1, p. 245.
114. W. Lehmann and H. Rinke, U. S. P. 2 852 494 (1958); Chem. Abs., 53, 1829 (1959).
115. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Pat. Application 662 307/23 (7th April, 1960).
116. V. V. Korshak, T. M. Frunze, L. V. Kozlov, and A. Yu. Alybina, Vysokomol. Soed., 2, 845 (1960).
117. D. J. Lyman and S. L. Jung, J. Polymer Sci., 40, 407 (1959).
118. V. V. Korshak, S. V. Vinogradova, and A. S. Lebedeva, Pat. Application 661 624/23 (31st March 1960).
119. V. V. Korshak, S. V. Vinogradova, and V. S. Artemova, Russ. P. 133 222 (29th August 1959).
120. V. V. Korshak and S. V. Vinogradova, Vysokomol. Soed., 1, 1482 (1959).
121. V. V. Korshak, T. M. Frunze, S. V. Vinogradova, L. V. Kozlov, and Wu Pang-yüan, Pat. Application 675 032/23 (30th July 1960).
122. A. A. Berlin and N. G. Matveeva, Uspekhi Khim., 29, 277 (1960).
123. F. W. Knobloch and W. H. Rauscher, J. Polymer Sci., 38, 261 (1959).
124. N. A. Glukhov, M. M. Koton, and Yu. V. Mitin, Vysokomol. Soed., 2, 791 (1960).

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RESERVE GALACTOMANNANS AND GLUCOMANNANS IN SEEDS, BULBS, AND RHIZOMES†

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I. INTRODUCTION

The great majority of plants contain starch reserves, although *Compositae* and *Gramineae* contain fructose polysaccharides as their main reserve carbohydrate. Other plant reserve polysaccharides have attracted little attention[1-3], but recently heteropolysaccharides, particularly galactomannans and glucomannans, have been studied successfully. The structure of known galactomannans and glucomannans has been further elucidated, and new compounds of this type have been discovered. These polysaccharides are of interest to industry as well as in terms of organic chemistry (in relation to their structure and properties) and comparative, or evolutionary, biochemistry. Some of them are foodstuffs, especially in oriental countries; on account of their high viscosity,

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others are used in the foodstuffs, pharmaceutical, paper, and tobacco industries, etc. Although such use is extensive abroad, especially in the USA, little attention has been paid in the Soviet Union to the extraction and use of these valuable compounds; the rich Soviet flora might well provide the excellent emulsifiers and gums, etc., needed by many industries.

This review considers work done on reserve galactomannans and glucomannans after 1952, earlier work being described in Whistler and Smart's monograph[4]. Industrially important galactomannans, recently reviewed[5-8], are described only shortly here.

II. NATURAL DISTRIBUTION OF GALACTOMANNANS AND GLUCOMANNANS

Appreciable quantities of galactomannans occur in the endosperm of bean seeds (*Leguminosae*), and smaller quantities in the seeds of palms (*Palmaceae*) and madder (*Rubiaceae*)[4]. Glucomannans have long been known as reserve polysaccharides in the tubers of different species of *Amorphophallus* (*Araceae*)[1], and in some orchids (*Orchidaceae*)[9,10]; they have recently been extracted from the bulbs of some lilies (*Liliaceae*) and from iris seeds (*Iridaceae*) (Tables 1 and 2, pp. 273 and 275). The heteropolysaccharides sometimes occur together with starch, as in lily bulbs, or they may appear as the sole reserve polysaccharide (*e.g.*, eremuran). They occur to varying extents, but some plants are very rich in them; about 35% of the seeds is composed of the galactomannans guaran and caroban, and the content of the glucomannan eremuran may be 30% of the dry weight of the rhizomes.

On account of insufficient study, the distribution of galactomannans and glucomannans is probably much wider than is now apparent. Some older data based on the separation of these heteropolysaccharides[9,10] should be checked, however, since inadequate procedures leave open the possibility that mixtures of homopolysaccharides, separable only with difficulty, were in fact obtained.

III. EXTRACTION AND PURIFICATION

Extraction with cold water or alkali, and precipitation with ethanol of varying concentration, is used to separate galacto- and gluco-mannans in dependence on solubilities. Monosaccharides and amino-acids are sometimes extracted first with methanol, the raw material then being dried. Galactomannans and glucomannans have for many years been purified through precipitation of their sparingly soluble copper complexes, formed when Fehling's solution is added to the polysaccharide solution, on account of the *cis*-hydroxyl group in the mannose residues. Special investigation showed that galactans, accompanying galactomannans in *Nux vomica*, remain in solution on such treatment[11]; it is hard to say whether such separation is generally complete. Fractionation of the polysaccharides of hemicellulose by means of barium hydroxide was recently proposed[12]; this forms complexes with galactomannans and glucomannans, apparently on account of the *cis*-hydroxyl groups therein. These complexes are soluble in dilute acids and water, but not in organic solvents or the cupric ethylenediamine complex. The separation of polysaccharides by means of Cetavlon‡ (cetyltrimethylammonium bromide) seems to be of great promise[13]; Barker and coworkers suggest that precipitation is due to interaction between Cetavlon and the borate complexes formed by the *cis*-hydroxyl groups of the mannose residues in mannans and galactomannans.

Although electrophoresis of neutral polysaccharides§ is described in the literature[14], this method has been used only recently for purifying and fractionating galactomannans and glucomannans; the electrophoresis of polysaccharides on fibreglass paper in an alkaline medium is of great interest[15]. The authors consider fibreglass paper to have an advantage over cellulose paper in that no complexes are formed between glass fibres and polysaccharides, so that the localisation of all types of the latter is facilitated. The great majority of the polysaccharides examined were heterogeneous; two components were found in the galactomannans in particular (guaran and another), while glucomannans such as konjac mannan and Iles mannan also appeared to be heterogeneous. Electrophoresis was conducted in a borate buffer (pH 9–10) or in 2 *N* NaOH or KOH solution, so that association of polysaccharide molecules was minimised. The movement of polymeric carbohydrates on glass paper apparently depends on the ionisation of hydroxyl groups under the influence of the alkaline electrolyte. It is difficult to evaluate such a separation briefly; unless some sort of artefact arises, such as an alkali-induced transformation, the indications produced of the heterogeneity of a series of polysaccharides will compel us to modify our concepts of their structure.

IV. PROPERTIES

Individual properties appear in Tables 1 and 2 and in the descriptions below of particular galactomannans and glucomannans; the following is only a general survey.

Solubility. Most galactomannans and glucomannans are soluble in cold or hot water or alkaline solutions, but a few have to be dissolved in concentrated sodium xylenesulphonate solution. Alkali, as in Fehling's solution used for purification, often induces loss of solubility. Solutions yield gels, or coagulate, on the addition of boric acid or salts of heavy metals[4]; a solution of konjac mannan coagulates on the addition of Congo red, and cools to a gel after being heated on the water-bath with this dye[16].

Viscosity. The high viscosity of solutions of some of these polysaccharides has been much studied recently, being the basis of their industrial use. Thus, the viscosity of guar sols is more than doubled on reaction with formaldehyde[17]; the viscosity of the gum from guar and acacia beans has been compared with that of other gums[18,19]; and

‡ On treatment of a mixture of 250 mg mannan and 250 mg glycogen with equal volumes of 10% Cetavlon solution and 1% borate buffer (pH 8.5), 204 mg of mannan separated, yielding only mannose on hydrolysis.

§ In 0.05 M borate buffer in Tiselius' apparatus, one of two components of yeast mannan had an electrophoretic mobility of 8.8×10^{-5} cm^2 V sec^{-1}, and the mannan A of stone walnut, $5.6 \times \times 10^{-5}$ cm^2 V sec^{-1}. Electrophoresis of the glucomannan eremuran was carried out in Tiselius' apparatus under the same conditions, in our laboratory (p. 277).

the viscosity and elasticity of konjac mannan gels after thermal treatment has been studied[20-22]. The viscosity of gums of the mannan type is lowered more than six times by boiling with aqueous hydrogen peroxide containing 50–90% of a lower aliphatic alcohol such as butanol or methanol, and a small quantity of sodium carbonate[23].

Infra-red absorption. Galactomannans and glucomannans have been studied little in this respect. Of the infra-red spectra of water-soluble gums, only those of acacia bean and guar flour gums have been obtained[24]. The infra-red spectrum of a glucomannan, of unspecified source, was described by Barker[25]. The author of the present article used infra-red spectroscopy in the study of the glucomannan eremuran, whereby fractions were identified and the presence of mannose and β-glycoside links was established (p.277).

Reaction with iodine. Indications appear in the literature that most galactomannans and glucomannans give no colour with iodine, but they are sometimes less positive, *e.g.* "the polysaccharide does not give a blue colour with iodine" (p.275). A glucomannan isolated by us, eremuran, gave a red-brown colour with iodine, showing beyond doubt that it was a heteropolysaccharide (p.277). Recently, the mechanism of the reaction between polysaccharides of the amylose type and iodine, involving a spiral structure, has become much clearer, but little is known yet with regard to branched polysaccharides, especially those having other than α-1,4-links. Earlier we established successfully a dependence of the iodine reaction on molecular weight, for a given degree of branching, for synthetic glycogens[26] and amylopectins[27]. Detailed study of the structures of some of the polysaccharides mentioned below may be a new basis for elucidation of the iodine reaction.

V. STRUCTURE

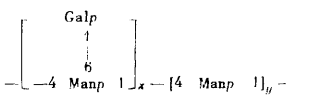
To elucidate the structures of galactomannans and glucomannans the usual polysaccharide methods are used; these give unusual results in only a few cases, where the configurational similarity of glucose and mannose epimers is involved.

Hydrolysis to the structural components is usually effected with sulphuric acid, or sometimes with formic acid; the resulting formic esters are then hydrolysed. The components are identified by paper chromatography (using as solvents butanol–ethanol–water, ethyl acetate–acetic acid–water, butanol–pyridine–water; etc.) or by means of crystalline derivatives such as mucic acid, mannose phenylhydrazone, and the glucoside of *p*-nitroaniline. Cellulose is normally used as adsorbent for the column chromatography of hydrolysates. The possible epimerisation of mannose and glucose must be borne in mind during analysis, especially if the latter is quantitative[28,29]. Polysaccharides methylated, as a rule, by repeated treatment with dimethyl sulphate and alkali, and then with methyl iodide, have recently been more uniformly fractionated by means of chloroform and hexane. Cleavage of the methylated polysaccharides is usually effected by methanolysis (2–5% HCl) and subsequent hydrolysis of the glycosides, or, less often, by hydrolysis with formic acid and subsequent hydrolysis of the esters. The methylated sugars are separated by paper chromatography in solvents such as butanol–ethanol–water or benzene–ethanol–water, or by chromatography on columns of cellulose and/or hydrocellulose in benzene–ethanol or butanol–ethanol–water. Corresponding methyl derivatives of glucose and mannose cannot usually be separated by chromatography; they are usually demethylated with hydrobromic acid, the free glucose and mannose being separated by chromatography or by paper electrophoresis[30,31], or as crystalline derivatives directly from their mixture. Thus, 2,3,6-tri-*O*-methylglucose crystallised from a trimethylhexose fraction after seeding, and after oxidation the mother-liquor yielded the phenylhydrazide of tri-*O*-methylmannonolactone. Estimations in such cases are based on optical activity. Alternatively, the whole of the mixture might be oxidised and the lactones separated by chromatography and converted to crystalline derivatives such as 2,3,6-tri-*O*-methylmannonamide[32]. Rebers and Smith[33] proposed a most interesting method involving the treatment of 2,3,6-tri-*O*-methylated mannose and glucose with cold methanolic hydrogen chloride; methyl 2,3,6-tri-*O*-methylglucofuranoside readily forms, and moves rapidly on the chromatogram. The planarity of the furanoside ring makes the conditions very unfavourable for formation of methyl 2,3,6-tri-*O*-methylmannofuranoside, with *cis*-methoxy groups at $C_{(2)}$ and $C_{(3)}$. According to Wickberg[34], methylated mannoses and glucoses may be separated by chromatography after acetylation of the free hydroxyl groups. Methylated sugars are usually estimated with hypoiodite. Data obtained by means of methylation are often verified by means of periodate oxidation, but continuous formation of formic acid is sometimes observed, and this method becomes invalid. Recently more study has been made of polyaldehydes, formed on the periodate oxidation of polysaccharides, and also of the polyalcohols which they yield on sodium borohydride reduction.

Optical activity and its modification by hydrolysis indicates the nature of α- and β-glycosidic links; infra-red spectra and enzymatic methods have found little application as yet in the study of glycosidic links in galactomannans and glucomannans.

Partial hydrolysis of polysaccharides, for the separation and identification of oligosaccharides, is usually effected by acetolysis after conditions have been established which give the maximum yield. Oligosaccharides are usually separated on carbon–Celite and cellulose columns. Control experiments are conducted to ensure that oligosaccharides have not formed by a partial reversion process during the hydrolysis of the polysaccharides.

Despite the widely differing galactose : mannose ratios, nearly all the galactomannans studied hitherto have much in common structurally; to a chain of mannopyranoside residues, with mainly glycosidic β-1,4-linkages, galactose residues are joined as end-groups, apparently mainly by α-glycosidic linkages¶:



(1)

Some exceptions are known, however. A few glucose end-groups may accompany the galactose residues as branches of the main polymannoside chain in the galactomannan of Kentucky coffee beans (p.274).

Glucomannans have been studied much less than galactomannans; oligosaccharides from particularly few polysaccharides have been separated and examined. The best

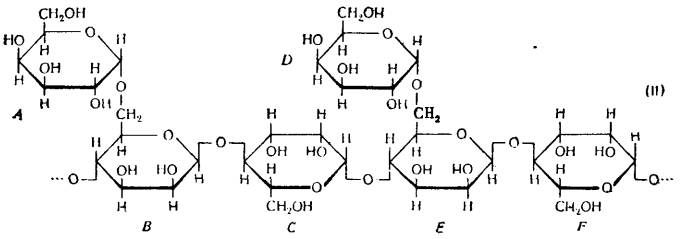
¶ *p* = pyranoside residue.

studied glucomannan from *Amorphophallus oncophillus* contains an unbranched chain of glucopyranoside and mannopyranoside residues, bonded mainly by β-1,4-glycoside linkages; the glucose residues are in groups of two or more (p.275), as apparently are the mannose residues. All the other glucomannans studied appear to be branched to varying extents; many β-1,4-glycoside linkages are found in most of them. The end-groups are mainly glucose residues in some glucomannans (lily bulbs, p.276), mainly mannose residues in others (*Licoris radiata* bulbs, p.276), and a combination of these in others (*Amorphophallus konjac*, p.275).

VI. INDIVIDUAL COMPOUNDS

A. Galactomannans (Table 1)

1. Guaran; this, one of the best studied galactomannans, constitutes about 35% of the endosperm of seeds of *Cyamopsis tetragonolobus* (*Leguminosae*), and is one of the most important industrial gums on account of its high viscosity[4]. It contains galactose and mannose in the ratio 1:2, the extent of branching in the molecule is indicated by the large quantity of formic acid formed on periodate oxidation. Tosylation confirms this result and indicates the presence of 1,6-branches. Investigation of the strength of guaran triacetate films, and X-ray examination of films of dry guaran, show the side-chains to be very short. The hydrolysis of trimethylguaran yielded equimolecular quantities of 2,3,4,6-tetra-*O*-methylgalactose, 2,3,6-tri-*O*-methylmannose, and 2,3-di-*O*-methylmannose. Soon after 1950 it was concluded from these data that guaran contained a polymannoside backbone with 1,4-linkages, a galactose residue being connected by a 1,6-linkage to every other mannose residue, on the average:



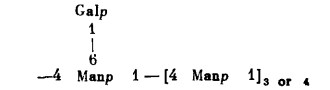
This structure was confirmed by partial acid and enzymatic hydrolyses, with subsequent separation of oligosaccharides and determination of their structure. Firstly, disaccharides were isolated: 4-*O*-β-D-mannosyl-D-mannose, apparently from the units *BC*(*EF*) or *CE*[35], and 6-*O*-α-D-galactopyranosyl-D-mannopyranose, apparently from *AB* and *DE*[36]. Trisaccharides were later also isolated; enzymatic hydrolysis of guaran† gave 65% of monosaccharide product and 7.5% of a crystalline mannotriose, *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranose[37], probably from units *BCE* or *CEF*. The structure of the triose was established by means of periodate oxidation, by partial hydrolysis to mannose and mannobiose, and by reduction to glycitol and acetylation. Finally, partial acid hydrolysis of guaran gave a 13.1% yield of a new crystalline trisaccharide, *O*-α-D-galactopyranosyl-(1→6)-*O*-β-D-mannopyranosyl-(1→4)-D-mannopyranose, from *ABC* and *DEF*; the structure of this has been demonstrated[38]. The fragment *CED*, while theoretically possible, has not yet been isolated, but the data given adequately confirm the above formula (I). As with the structure of other carbohydrate polymers, it must be asked to what extent the proposed formula, based on mean results for many molecules, represents the structure of the single molecule with respect to the regularity of branching. Study of the mechanism of this polysaccharide's biosynthesis may clarify this problem. The molecular weight of guaran triacetate is 220 000 (osmometer)[4].

TABLE 1. Galactomannans.*

Source: family	Source: species	Source: part of plant	Name	$[\alpha]_D$	Galactose:mannose ratio	$[\alpha]_D$ of methylated derivative	References
1 *Leguminosae*	*Cyamopsis tetragonolobus* (guar)	seeds	guaran	+53° (NaOH solution)	1:2	+42° (chloroform)	36,37,38
2 »	*Ceratonia silique*	»	caroban		1:3—4 (impure)		4
3 »	*Trigonella foenum graecum* (fenugreek)	»		+70°±10° (water)	5:6		11,39,40
4 »	Lucerne (var. *provensa*)	»		+118°±11° (water)	4:5	+66°±3° (chloroform)	41,40
5 »	*Trifolium pratense*	»		+78°±11° (water)	7:9	+76°±2° (chloroform)	41
6 »	*Gymnocladus dioica* (Kentucky coffee bean)	»		+29° (water)	1:4	0° (acetone)	43
7 »	*Glicina hispida*	bean husks		+63° (water)	2:3	+58°	44
8 *Palmaceae*	*Borassus flabillijer L.*	seeds of fruit		—	1:2.83		45

* All the galactomannans were purified by means of copper complexes except 6, which was purified by means of the acetyl derivative.

2. Caroban; this, the galactomannan of acacia beans, *Ceratonia siliqua* (*Leguminosae*), constitutes about 88% of commercial gum, of which the beans contain about 35%. Commercial locust bean gum, known also as pigs' bread, etc., is of wide industrial application in countries such as the USA. Reports of the galactose:mannose ratio differ from 27:73 to 14:86.[4] Hydrolysis of fully methylated caroban yielded 2,3,4,6-tetra-*O*-methylgalactose (1 mole), 2,3,6-tri-*O*-methylmannose (between 2 and 4 moles reported), and 2,3-di-*O*-methylmannose (1 mole)[4]. These data, and those from periodate oxidation, indicate that caroban is a polymannoside, like guaran, but with few galactose residue side-chains:

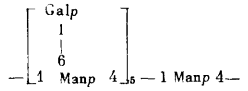


The molecular weight of caroban is 310 000.[4]

3. The galactomannan from fenugreek seeds (*Trigonella foenum graecum*), extracted in 1932 by Daoud[39], was recently examined carefully by Andrews and coworkers[11]. The galactomannan, comprising 13.6—15% of

† The fraction of the enzyme from germinating guar seeds was used which was precipitated by 20—30% ammonium sulphate solution.

these seeds, was extracted with cold water and purified by means of the copper complex. Crystalline galactose and mannose were obtained in the ratio 5 : 6. Hydrolysis after complete methylation yielded 2, 3, 4, 6-tetra-*O*-methylgalactose, 2, 3-di-*O*-methylmannose, and 2, 3, 6-tri-*O*-methylmannose in the ratio 5 : 5 : 1. The tetra-*O*-methylgalactose was identified chromatographically and also characterised as the anilide; the methylmannoses were characterised, after oxidation with bromine water, as the crystalline lactones and as the hydrazides of the corresponding acids. Periodate oxidation confirmed these results, the yield of formic acid indicating 43.6% of end-residues (methylation gave 43.3%). This galactomannan is therefore similar in general structure to guaran and caroban, having a polymannoside chain with 1, 4-links, to the $C_{(6)}$ atoms of which galactose residues are connected through $C_{(1)}$, forming short side-chains or end-groups. The difference from guaran lies in the greater degree of branching and the greater content of galactose end-groups. A possible structure is:



supported[40] by the partial acid hydrolysis of the compound to the following oligosaccharides. (*a*) 4-*O*-β-D-mannopyranosyl-D-mannose, (*b*) 6-*O*-α-D-galactopyranosyl-D--mannose, and (*c*) the mannotriose *O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranosyl-(1 → 4)-D-mannose.

4. The galactomannan from lucerne seeds (*Provensa*) was obtained in a yield of about 5.5% by extraction with hot water[41], and purified by means of the copper complex. Its aqueous solution gives no colour with iodine. Galactose and mannose are contained in the ratio 4 : 5. Methylation and hydrolysis yielded 2, 3, 4, 6-tetra--*O*-methylgalactose, 2, 3, 6-tri-*O*-methylmannose, and 2, 3-di-*O*-methylmannose in the ratio 4 : 1 : 4, the methylated sugars being separated on a hydrocellulose column and identified as crystalline derivatives. The extent of branching is very large, almost every residue in the polymannoside chain having a gelactose residue as a branch from $C_{(6)}$. Periodate oxidation indicated 43.7% galactose end-residues (methylation gave 44.2%). About 10% of unchanged mannose was found in the hydrolysate of the galactomannan after "complete" periodate oxidation, indicating that in a highly branched structure periodate has less easy access to the mannose residues, and oxidation of these at $C_{(2)}$ and $C_{(3)}$ is slower. More prolonged attack of an excess of $NaIO_4$ at pH 7 oxidised the mannose fully, the resultant data then agreeing exactly with those obtained by methylation. A possible structure for this compound is:

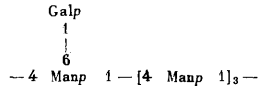


Recent partial acid hydrolysis of this compound yielded the crystalline oligosaccharides: 4-*O*-β-D-mannopyranosyl--D-mannose, 6-*O*-α-galactopyranosyl-D-mannose, and *O*-β-D-mannopyranosyl-(1 → 4)-*O*-β-D-mannopyranosyl--(1 → 4)-D-mannose. This supports the above structure and refines our conception of the character of glycosidic bonds[40].

In 1947 extraction of another lucerne (*Medicago sativa*) with hot 10% NaOH solution yielded a galactomannan with a unique high galactose content, twice as large as its mannose content[42]. Data from methylation implied that half the galactose constitutes all the end-residues and the rest enters with the mannose into the backbone. However, the compound was later shown to be a polysaccharide mixture, largely composed of a galactomannan similar in structure to guaran[42a].

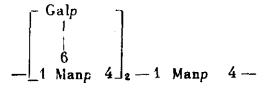
5. The galactomannan from clover seeds (*Trifolium pratense*), extracted with hot water and purified by means of the copper complex, is very similar to that from lucerne (*Provensa*)[41]. The galactose : mannose ratio is 7 : 9. Methylation and hydrolysis yields 2, 3, 4, 6-tetra--*O*-methyl-D-galactose, 2, 3, 6-tri-*O*-methyl-D-mannose, and 2, 3-di-*O*-methyl-D-mannose in the ratio 7 : 2 : 7. Thus, as with the *Provensa* galactomannan, almost every residue in the polymannoside chain bears a galactose residue branch, bonded by a 1, 6-link. No oligosaccharides were obtained from this compound.

6. The galactomannan from Kentucky coffee bean seeds (*Gymnocladus dioica*) was extracted with alkali and purified as the acetate[43]. Viscous solutions of the compound give precipitates with Fehling's solution, and gels with small amounts of borax. Galactose and mannose, identified as the methylphenylhydrazone and the phenylhydrazone respectively, are contained in the ratio 1 : 4. Methylation and hydrolysis yields 2, 3, 4, 6-tetra-*O*-methyl--D-galactose (1 mole), 2, 3, 6-tri-*O*-methyl-D-mannose (3 moles), 2, 3-di-*O*-methylmannose (1 mole), and 3.3% 2, 3, 4, 6-tetra-*O*-methylmannose. A possible unit for the main part of this compound is:



The 2, 3, 4, 6-tetra-*O*-methylmannose may arise from the end-residue of the polymannoside chain, but its percentage would then imply a chain of about 30 residues, and therefore reducing properties, which are not in fact observed. It is therefore more likely that on the average one mannose end-group per thirty hexose residues accompanies the galactose end-groups. Periodate oxidation supports this, one molecule of formic acid appearing per five hexose residues with the adsorption of 6 moles of periodate.

7. The galactomannan from soya-bean husks; the husks, after extraction with acetone, are then extracted with water at 40°. The product obtained in 2% yield is purified as the copper complex[44]. Crystalline galactose and mannose are obtained in the ratio 2 : 3, (compare 1 : 2 in purified guaran, 2 : 3 in impure guaran). 2, 3, 4, 6-tetra--*O*-methylgalactose, 2, 3, 6-tri-*O*-methylmannose, and 2, 3, -di-*O*-methylmannose are obtained from the methylated compound in the ratio 2 : 1 : 2. These data imply a polymannoside backbone as in guaran and other galactomannans, with two 1, 6-linked galactose branches to every three 1, 4--linked mannose residues, on the average:



Such a structure should need 1.4 moles periodate per anhydrohexose unit, to give 0.4 mole formic acid; the actual quantities are 1.2 moles and 0.37 mole. The authors suggest the presence of β-links in the polymannoside chain, and the α-configuration of the galactose residues. The polysaccharide has a molecular weight of 32 000, much lower than that of guaran.

8. The galactomannan from palm-fruit kernels (*Borassus flabellijer* L.) was obtained[45] by extraction with hot 10% NaOH solution after the raw material had been dehydrated, treated with 80% alcohol to remove free sugars, and dried. The polysaccharide, purified by means of its copper complex, was hydrolysed; the galactose and mannose, produced in the ratio 1 : 2.83, were identified chromatographically and by conversion into mucic acid and a phenylhydrazone respectively. The structure of the polysaccharide was not investigated.

Glucomannans from *Amorphophallus* species of the *Araceae* family are the best known, but there is not yet sufficient proof that they are not mixtures of homopolysaccharides.

B. Glucomannans (Table 2)

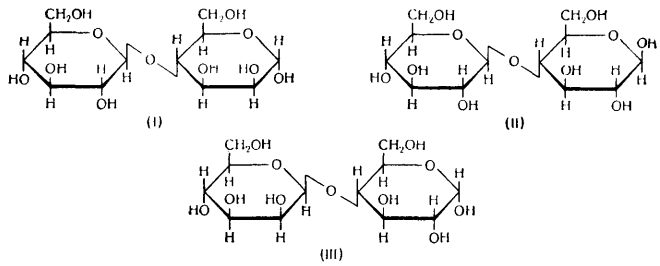
1. The glucomannan from tubers of *Amorphophallus oncophillus*, plants growing in Indonesia, etc.; flour containing about 40% by dry weight of polysaccharides is prepared from these tubers. It was shown in 1954 that Iles mannan, extracted from these tubers, is a mixture of a glucomannan and a polyglucosan, resembling amylose, in a ratio of about 6 : 1.[33] On account of the low solubility of the glucomannan in water and NaOH solution, it was dissolved in 50% sodium xylenesulphonate solution; the resultant gel dissolved in 30% aqueous NaOH to give a solution stable to dilution and to neutralisation with acetic acid. The glucomannan may be fractionally precipitated from the diluted alkaline solution with Fehling's solution, the polyglucosan remaining dissolved. The glucomannan thus obtained is stable in aqueous solution, but polysaccharide is deposited on boiling; it gives no blue colour with iodine. A more complete separation of the polysaccharides was effected by methylation and subsequent repeated recrystallisation from ethanol or acetone; as the solvent cooled, the solid separating was richer than the solution in the methylated glucomannan. Hydrolysis of the latter was slow, indicating the pyranoside nature of the hexose residues, and gave a mixture of 2,3,6-tri-*O*-methylglucose and 2,3,6-tri-*O*-methylmannose, inseparable by chromatography. The ready conversion of the glucose derivative to the methyl glucofuranoside afforded a separation, since the non-reducing methyl 2,3,6-tri-*O*-methylglucofuranoside moved faster on a hydrocellulose–cellulose column than did the 2,3,6-tri-*O*-methylmannose mixed with it. Both trimethylhexoses were identified by means of their rotatory power and the formation of crystalline di-*p*-nitrobenzoates. The 2,3,6-tri-*O*-methylglucose : 2,3,6-tri-*O*-methylmannose ratio, and hence the ratio of the free sugars in the hydrolysate, was 1 : 2. The absence of di- and tetra-methylhexoses shows this glucomannan to be an unbranched chain with 1,4-glycoside links; the increased rotation on hydrolysis indicates the predominance of β-glycoside links. The following structures are therefore possible:

$$-[1\beta D\ Manp\ 4\text{—}1\beta D\ Manp\ 4\text{—}1\beta D\ Gp\ 4]_n- \quad (A)$$

$$-[1\beta D\ Gp\ 4\text{—}]_2-[1\beta D\ Manp\ 4]_4 \quad (B)$$

$$-[1\beta D\ Gp\ 4\text{—}1\beta D\ Manp\ 4]_2-[1\beta D\ Manp\ 4]_2 \quad (C)$$

Recently, acetolysis of the glucomannan under special conditions‡ gave a mixture from which three crystalline disaccharides were separated[46]: (1) 4-*O*-β-D-glucopyranosyl-*O*-α-D-mannopyranose (I, below), identified by means of its physical constants, by oxidation with bromine water and hydrolysis to glucose and mannonic acid, and by conversion to an octa-acetate; (2) cellobiose (II, below), identified by means of its physical constants, by conversion to an octa-acetate, and by the action of β-glucosidase to give glucose alone; and (3) 4-*O*-β-D-mannopyranosyl-*O*-α-D-glucopyranose (III, below). The structure of the last new disaccharide was partly established by oxidation with bromine and hydrolysis, to give mannose and gluconic acid, and by methylation and hydrolysis to give 2,3,4,6-tetra-*O*-methylmannose and 2,3,6-tri-*O*-methylglucose:



(I) (II)

(III)

If the units represented by (I)–(III) above are repeated regularly, then these results force us to reject (A) and (C) (since cellobiose was obtained) in favour of (B), replication of which makes production of all three disaccharides possible. (B) should, however, give rise to mannobiose and mannotriose, which have not yet been found. The authors assume the links between mannose units to be broken more readily than the others on acetolysis. (B) may be accepted, or other structures sought, on the results of searches for other oligosaccharides in acetolysis and hydrolysis products.

2. The glucomannan from tubers of *Amorphophallus konjac* (or *Conophallus konjac* Schott), known for

TABLE 2. Glucomannans.*

Source			Name	$[\alpha]_D$	Glucose: mannose ratio	$[\alpha]_D$ of methylated derivative	References
family	species	part of plant					
Araceae	*Amorphophallus oncophillus*	tubers		−21.3° (water)	1 : 2	−41° (chloroform)	33,46
»	*Amorphophallus konjac*	»	konjac mannan	−38° (water)	2 : 3	−19° (chloroform)	4,49,50
Liliaceae	*Lilium candidum*	bulbs	—	−26°	1 : 1.83	—	32
»	*L. henrii*	»	—	−21°	1 : 1.93	−23°	32
»	*L. umbellatum*	»	—	−25°	1 : 2.00	−20°	32
Amaryllidaceae	*Licoris radiata*	»	khiganbana mannan	—	1 : 4	−30.46° (chloroform)	52,53
Liliaceae	*Eremurus regelii*	rhizomes	eremuran	−30°±2° (0.1 *N* NaOH)	1 : 2	−37°±6° (water)	54–57
Iridaceae	*Iris ochroleuca*	seeds	—	−25°±2° (2*N* NaOH)	1 : 1**	−9° (chloroform)	58
»	*I. sibirica*	»	—	−26°±3° (2*N* NaOH)	1 : 1**	−11.1° (chloroform)	58

* All the glucomannans were purified by means of copper complexes.

** These polysaccharides contained 97% and 98% of (glucose + + mannose) and 1–2% of galactose (p. 277).

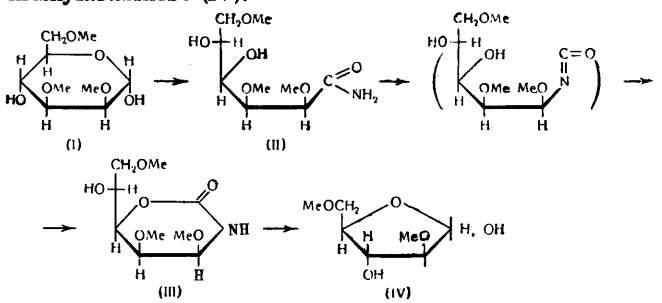
‡ Under these conditions a 30% yield of oligosaccharides was obtained.

many years as "konjac mannan"; this is the main polysaccharide in "konjac flour", prepared from the macerated, dried, and ground tubers[4] and widely used for food in Japan and other countries. The polysaccharide may be extracted with water[4] at 1.5 atm. Preliminary study, mainly by Japanese workers, showed the glucose : mannose ratio in konjac mannan to be 1 : 2, although it may vary. The action of spore-bearing bacteria from "konjac flour" on the mannan yielded the polysaccharide levidulin, consisting of one glucose to two mannose residues[47]. A similar or identical trisaccharide, named levidulinose, was obtained by the action of Taka-diastase[48], and the acetolysis of konjac mannan yielded a similar trisaccharide[49]. For none of these trisaccharides was a structure established. Hydrolysis of methylated konjac mannan yielded 2,3,4-tri-*O*--methylglucose, 2,3,4-tri-*O*-methylmannose, and 2,3,6--tri-*O*-methylmannose; on this basis a structure was suggested involving an unbranched chain with a predominance of 1,6-links[49].

Recent studies[50] have utilised hitherto inaccessible techniques. Hydrolysis of the polysaccharide, purified by means of the copper complex, gave glucose and mannose in the ratio 2 : 3§. Methanolysis and hydrolysis of the fully methylated glucomannan yielded 2,3,4,6-tetra-*O*-methylglucose, 2,3,4,6-tetra-*O*-methylmannose, 2,3,6-tri-*O*--methylglucose, 2,3,6-tri-*O*-methylmannose, 2,6-di-*O*--methylglucose, and, apparently, 2,6-di-*O*-methylmannose. The ratio, tetra- : tri- : di-methylhexose was 1 : 11 : : 1, indicating a mean chain length of approximately 13; the ratio tetramethylglucose : tetramethylmannose was 2 : 3, in agreement with the ratio of the free sugars in the hydrolysate of the initial polysaccharide. The tetramethylhexoses were not separable, but after demethylation with hydrobromic acid the free sugars were easily separated by chromatography and electrophoresis on paper. The trimethylhexoses and dimethylglucose were identified by means of the di-*p*-nitrobenzoates and the trinitrobenzoate respectively.

These data are not in accordance with the structure based on earlier work by Nishida[49]; the polysaccaride is branched, not linear, with mannose as well as glucose residues as end-residues; 1,4-glycoside links, not 1,6--links, predominate in the backbone; the low rotatory power of konjac mannan and its methylated derivative imply that they are β-links. This new structure, based on methylation studies, is supported by: (1) data from periodate oxidation; the chain length was found to be 11, some hexose residues at the branching point being unoxidised; and (2) study of hydrolysis products from the polyalcohol, obtained by sodium borohydride reduction of the polyaldehyde to which konjac mannan is oxidised by periodate. The ratio of glycerol, formed from end-residues, to erythritol, formed from hexose residues between branching points, was 1 : 15.

3. The glucomannan from lily bulbs, comes from three types[32]: *Lilium candidum*, *L.henrii*, and *L.umbellatum*; macerated bulbs were treated with methanol to remove mono- and oligosaccharides and amino-acids, dried, and ground. The glucomannans were extracted with cold water, and precipitated and reprecipitated with alcohol. The yields, based on the dry weight of the bulbs, were 14% from *L.candidum*, 20% from *L.henrii*, and 5% from *L.umbellatum*. After purification by means of the copper complex, the glucomannans were insoluble in water, but soluble in sodium hydroxide solution and formic acid; they gave no colour with iodine. Hydrolysis of all three polysaccharides give glucose and mannose in the approximate ratio 1 : 2. Exhaustive methylation of the polysaccharides from *L.umbellatum* and *L.henrii* gave yields of 56% and 34% respectively of the methylated derivatives. Methanolysis of the trimethylglucomannans and hydrolysis of the glycosides formed gave mainly trimethylhexoses and very small amounts of tetra- and dimethylhexoses. The trimethylhexoses were not separable by chromatography, but from its rotation the mixture appeared to contain 2,3,6--tri-*O*-methyl derivatives of glucose and mannose in the ratio 1 : 2. Separation was achieved by oxidation to the corresponding lactones, which were separated on cellulose and converted to crystalline derivatives. Thus, 2,3,6--tri-*O*-methylmannose (I, below) was characterised as the crystalline 2,3,6-tri-*O*-methylmannonamide (II), which hypochlorite cleaved to a crystalline derivative of the cyclic ureide (III). Later hydrolysis gave 2,5-di-*O*--methylarabinose (IV).



On methylation, the glucomannan from *L.umbellatum* yielded 3.7% of tetramethylhexoses, that from *L.henrii* yielded 1.3%. The tetramethylhexose fraction appeared to be mainly 2,3,4,6-tetra-*O*-methylglucose, identified in particular in the crystalline form and by convertion to crystalline *N*-phenyl-D-glucopyranosylamine tetramethyl ether. It must be borne in mind that after demethylation of the tetramethylhexoses a trace of mannose was detected chromatographically together with the glucose.

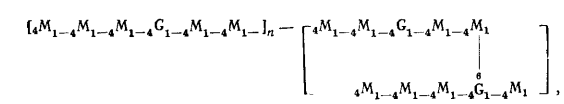
The dimethylhexose from the trimethylglucomannan of *L.umbellatum* was mainly 2,4-di-*O*-methylglucose; that from *L.henrii* was a mixture of glucose and mannose derivatives, but the quantities obtained of these were too small for exact characterisation. These data show the glucomannans of *L.umbellatum* and *L.henrii* to be fairly similar; the slightly branched chains of each are composed of glucopyranosyl and mannopyranosyl residues in the ratio 1 : 2, joined by β-1,4-glycoside links. The non--reducing end-residues are mainly of glucose. The branching-points in the glucomannan from *L.umbellatum* are apparently glucose residues linked at $C_{(1)}$, $C_{(3)}$, and $C_{(6)}$. The mean chain length of the glucomannan from *L.umbellatum* is 27 hexose units; for that from *L.henrii*, it is 75 hexose units.

Periodate oxidation was fruitless on account of the continuous production of formic acid.

4. The glucomannan from *Licoris radiata* bulbs; this, also called "Khiganbana mannan" from the Japanese name for the plant, was isolated and examined by Hayashi and coworkers[52]. Water extraction and purification by means of the copper complex gave a yield of about 2% of pure product, based on the dry weight of the bulbs. Acid hydrolysis[52] gave glucose and mannose in the ratio 1 : 4.

§ Thus, indications of glucuronic acid in konjac mannan were not confirmed[51].

Methylation and hydrolysis gave 2,3,6-tri-*O*-methylmannose (66.2%), 2,3,6-tri-*O*-methylglucose (13.9%), 2,3,4,6-tetra-*O*-methylmannose (11.3%), and 2,3-di-*O*-methylglucose (8.6%). Partial hydrolysis yielded mannobiose, mannotriose, glucomannotriose, and glucomannotetrose. From these data, and periodate oxidation, Mizuno and Hayashi[53] proposed this structure:



M and G denoting mannose and glucose residues; $n \simeq 49$. The difficulty of access to the original report precludes knowledge of methods used to separate and identify the methylated sugars, etc.

5. The glucomannan from *Eremurus regelii* rhizomes; this, eremuran, was separated by us[54] by means of extraction with cold water from the dried and ground roots, precipitation with alcohol, and reprecipitation from 5% trichloroacetic acid with alcohol. The eremuran content in roots of plants growing in Central Asia exceeds 30% of the dry weight. Very viscous solutions of this polysaccharide give with iodine a red coloration with an absorption maximum at 530 mμ, near to that of rabbit liver glycogen (500 mμ) but much less intense. The components are glucose (1 mole) and mannose (2 moles), which were identified crystallographically, by conversion to crystalline mannose phenylhydrazone and the *N*-glucoside of *p*-nitroaniline, and by fermentation with special strains of yeast. The homogeneity of eremuran was investigated by fractionation with ethanol, by electrophoresis[55,65], and by deposition of the copper complex. Fractions were obtained by precipitation with one and two volumes of alcohol respectively; they differed in reducing power and intensity of coloration with iodine, but had identical glucose and mannose contents and identical infra-red spectra. They were, therefore, apparently, homologues of different degrees of polymerisation. Electrophoresis in a borate buffer in Tiselius' apparatus yielded two components, of which the faster-moving constituted most of the polysaccharide and contained glucose and mannose. The other component has not yet been investigated on account of the very small quantities available. Eremuran, precipitated as the copper complex and then regenerated, still contains glucose and mannose in the ratio 1 : 2, but becomes insoluble in water, probably on account of the changed conformation of the hexose residues. The flocculent aqueous suspension gives a dark red-brown colour with iodine, however. Eremuran is not hydrolysed by α- and β-amylases. Methylation of eremuran or its tetra-acetate yields di-, tri-, and tetra-methylhexoses. Preliminary data indicate the quantity of trimethylhexoses to exceed that of the tetramethylhexoses by more than ten times; a mixture is obtained of 2,3,6-tri-*O*-methylglucose and tri-*O*-methylmannose. The di- and tetra-methylhexoses have not yet been identified.

Partial hydrolysis of eremuran yields three oligosaccharides, one of which is a disaccharide consisting of glucose and mannose residues and apparently being 4-β-glucopyranosidylmannose; its structure is being studied. The data so far available therefore indicate that eremuran is a branched polysaccharide with a backbone of glucose and mannose residues, mainly joined by 1,4-glycoside links. Optical activity and infra-red data[57] indicate that these are β-links.

On account of the rich supply of *Eremurus*, eremuran has great economic potentiality for the Soviet Union as (*a*) an emulsifier as good as gum arabic, (*b*) a source of mannose, which is imported at present, and (*c*) as a possible substitute for blood, after partial hydrolysis.

6. The glucomannan of iris seeds; Andrews and coworkers[58] investigated *Iris ochroleuca* and *I.sibirica*. The polysaccharides were extracted with 10% NaOH solution, precipitated with alcohol, and purified by means of the copper complex and repeated precipitation with alcohol. They gave no blue colour with iodine. Both polysaccharides were hydrolysed to approximately equal quantities of glucose and mannose, comprising 97% of the polysaccharide from *I.ochroleuca* and 98% of that from *I.sibirica*. The remainder was galactose; it is not certain whether this is a component of the polysaccharides, or whether some galactomannan impurity remained despite purification. Methanolysis of the trimethylated polysaccharides gave tetra-, tri-, and di-methylhexoses in the ratio 1 : 24 : 1.3 for *I.ochroleuca* and 1 : 30 : 0.8 for *I.sibirica*. The trimethyl derivatives formed a mixture, inseparable by chromatography, of 2,3,6-tri-*O*-methylglucose, identified in the crystalline form, and 2,3,6-tri-*O*-methylmannose, identified as the phenylhydrazide of trimethylmannonolactone. The tetramethylhexoses (3 and 3.2%) were largely 2,3,4,6-tetra-*O*-methylgalactose, with small amounts of glucose and mannose derivatives. The dimethylhexoses were mainly mannose and glucose derivatives, but were not fully identified. These data indicate that both polysaccharide chains are little branched, and are composed of glucose and mannose residues with 1,4-links. All the galactose is present as end-residues, and may be part of an admixture of galactomannan. The methylation data, and reducing power, show the polysaccharide from *I.ochroleuca* to have a significantly higher molecular weight than that from *I.sibirica*.

7. The polysaccharides from seeds of the Japanese kaki tree (*Diospyros kaki*) were obtained by Hayashi[59] by means of extraction with hot water and then with 5% NaOH solution. The two fractions thus obtained were purified by means of the copper complexes. Both contained mannose (predominantly), glucose, and a little pentose. It is not certain whether this polysaccharide is a glucomannan containing some pentose, or a "pentoglucomannan" as the authors suggest. Triacetyl derivatives of both polysaccharides have been made.

VII. DERIVATIVES

The 2-cyanoethyl ethers of galacto- and gluco-mannans and the carboxymethyl ether of guaran[60] have been obtained; they form very stable gels with salts of heavy metals[61]. A patent exists for the etherification of galacto- and gluco-mannans with di-2-chloroethyl ether and a dihalogenohydrin derived from glycerol, the residues of which cross-link polysaccharide molecules[62]; the products are very viscous.

The conditions needed to produce nitro-derivatives of konjac mannan, and their properties, have been studied[63].

VIII. SOME BIOCHEMICAL PROBLEMS

Although the biological significance of galacto- and gluco-mannans as reserve carbohydrates, disappearing as

the seeds grow, is realised, the mechanism of the biosynthesis and cleavage of these compounds is hardly known. Saccharose and raffinose were detected in a study of lucerne seeds[40], and it was therefore suggested that during galactomannan synthesis galactopyranosyl residues from raffinose were converted into a polymer of mannose; and that cleavage of galactomannans involved conversion of these residues into saccharose. On this hypothesis, the synthesis of galactose end-residues is a way of "reserving" the highly mobile galactose. The established variation of galactose content in glucomannans accords with the hypothesis[41]. The presence of guanosine diphosphate mannose in yeasts[64] and its possible role in the synthesis of yeast mannans suggests a similar synthesis of the polymannoside backbone in plant galactomannans and, possibly, glucomannans.

The high content of galactomannan-cleaving enzymes in germinating guar seeds[38] was used to hydrolyse guaran to oligosaccharides, but no attempt was made to fractionate the enzymes. An impure enzyme hydrolysing konjac mannan was apparently isolated[65]. In the human body 95.5% of konjac mannan is digested, but this occurs by virtue of intestinal bacteria, since pancreatic extract has no effect on mannans[66].

Caroban and guaran have the interesting property, along with some other galactans and other polysaccharides containing galactose residues, of serological activity; they precipitate the antibodies of antipneumococcus serum (type XIV)[67].

IX. APPLICATION

This has been mentioned above (p.271); a series of reviews deals with the industrial use of some galacto- and gluco-mannans. In ripe seeds there have recently been found, galactomannans able to replace caroban, the demand for which is not fully satisfied[69]. The treatment of seeds containing galactomannans to give good raw materials for industrial glues has been described[70,71]. The preparation of "dry", rapidly swelling galactomannan gums is described in a patent[72]. A comparative study of guar gums, with particular reference to viscosity, is described[73] (see also p.271), as is a comparison of galacto- and gluco-mannan "slimes"[74]. A number of works deal with the use of galactomannan gums in the paper industry[75,76], particularly together with starch[77]; their great use in the tobacco industry is also demonstrated[78,79]. Their use has been suggested in pharmacy for preparing gels[80] and as thickeners[81]. Their use in the food industry[82] has led to development of methods of food analysis for galactomannans[83,84].

1. W. Pigman (Editor), "The Carbohydrates: Chemistry, Biochemistry, Physiology", Academic Press, New York, 1957.
2. F. Micheel, "Chemie der Zucker und Polysaccharide", 2 Aufl., Akademische Verlag., Leipzig, 1956.
3. W. Ruhland, "Handbuch der Pflanzenphysiologie", B. VI, Akademische Verlag., Berlin, 1958.
4. R. L. Whistler and C. L. Smart, "Polysaccharide Chemistry", Academic Press, New York, 1953.
5. R. L. Whistler and J. Miller, "Industrial Gums", Academic Press, New York, 1959.
6. R. L. Whistler, "Natural Plant Hydrocolloids", Advances in Chemistry Series (Amer. Chem. Soc.), 11, 45 (1954).
7. H. Deuell and H. Neukom, *ibid.*, p. 51.
8. H. Deuell, J. Solms, and H. Neukom, Chimia (Switz.), 8, 64 (1954).
9. S. Otsuki, Acta Phytochim., Tokyo, 10, 29 (1937).
10. Y. Kihara, J. Agric. Chem. Soc. Japan, 7, 1061 (1931).
11. P. Andrews, L. Hough, and L. K. Jones, J. Chem. Soc., 2744 (1952).
12. H. Meier, Acta Chem. Scand., 12, 144 (1958).
13. S. Barker, M. Stacey, and G. Zweifel, Chem. and Ind., 330 (1957).
14. D. Northcote, Biochem. J., 58, 353 (1954).
15. B. A. Lewis and F. Smith, J. Amer. Chem. Soc., 79, 3929 (1957).
16. H. Torigata, J. Chem. Soc. Japan, 73, 485 (1952).
17. W. Jordan, U. S. P. 2 730 505 (Jan., 1956); Chem. Abs., 50, 5316h (1956).
18. P. Davis, Chem. Processing, 20, No. 1, 208 (1957).
19. J. Schlakman and A. Bartilucci, Drug Standards, 25, 149 (1957).
20. H. Torigata, J. Chem. Soc. Japan, 72, 378 (1951).
21. H. Torigata, J. Chem. Soc. Japan, 73, 157 (1952).
22. N. Hirai, Chem. Abs., 46, 5402g (1952).
23. J. Opie and R. Hamilton, U. S. P. 2 767 167 (1956); Chem. Abs., 51, 2316c (1957).
24. S. Newburger, J. Jones, and G. Clark, Proc. Sci. Toilet Goods Assoc., 19, 25 (1953).
25. J. Barker, J. Chem. Soc., 3468 (1954).
26. B. N. Stepanenko, "Preparativnyi Sintez Glikogena *in vitro* s Pomoshch'yu Myshechnykh Enzimov i Izuchenie Sintetich-eskikh Glikogenov" (Preparation of Glycogen *in vitro* by Means of Muscle Enzymes and Study of the Synthesised Glycogens), Communications and Reports at the Third International Biochemical Congress, Brussels, 1955.
27. B. N. Stepanenko and E. M. Afanas'eva, Biokhimiya, 22, 305 (1957).
28. A. Roudier and L. Eberfeld, Mem. Services chim. État, 37, 231 (1952).
29. A. Roudier and L. Eberfeld, Mem. Services chim. État, 40, 261, 285 (1955).
30. L. Hough, J. K. Jones, and W. Wadman, J. Chem. Soc., 1702 (1950).
31. F. Smith and H. Srivastava, J. Amer. Chem. Soc., 81, 1715 (1959).
32. P. Andrews, L. Hough, and J. K. Jones, J. Chem. Soc., 181 (1956).
33. P. Rebers and F. Smith, J. Amer. Chem. Soc., 76, 6097 (1954).
34. B. Wickberg, Acta Chem. Scand., 12, 615 (1958).
35. R. L. Whistler and J. Stein, J. Amer. Chem. Soc., 73, 4187 (1951).
36. R. L. Whistler and D. Durso, J. Amer. Chem. Soc., 73, 4189 (1951).
37. R. L. Whistler and C. Smith, J. Amer. Chem. Soc., 74, 3795 (1952).
38. R. L. Whistler and D. Durso, J. Amer. Chem. Soc., 74, 5140 (1952).
39. K. M. Daoud, Biochem. J., 26, 255 (1932).
40. M. Henderson, L. Hough, and P. Painter, J. Chem. Soc., 3519 (1958).
41. P. Andrews, L. Hough, and J. Jones, J. Amer. Chem. Soc., 74, 4029 (1952).
42. E. L. Hirst, J. K. Jones and Walder, J. Chem. Soc., 1443 (1947).
42a. R. McCredie, Diss. Abs., 19, 432 (1958).
43. E. Larson and F. Smith, J. Amer. Chem. Soc., 77, 429 (1955).
44. R. L. Whistler and J. Saarnio, J. Amer. Chem. Soc., 79, 6055 (1957).
45. V. Subrahmanyan, G. Bains, C. Natarijan, and D. Bhatia, Arch. Biochem. Biophys., 60, 27 (1956).

46. F. Smith and H. Srivastava, J. Amer. Chem. Soc., 78, 1404 (1956).
47. T. Mayeda, J. Biochem. (Japan), 1, 131 (1922).
48. S. Ohtsuki, Acta Phytochim., Tokyo, No. 1, 1 (1922).
49. K. Nishida and H. Hashima, J. Dept. Agr. Kyushu Imp. Univ., 2, 277 (1930).
50. F. Smith and H. Srivastava, J. Amer. Chem. Soc., 81, 1715 (1959).
51. H. Torigata, J. Chem. Soc. Japan, Pure Chem. Sect., 73, 533 (1952); Chem. Abs., 48, 1969d (1954).
52. K. Hayashi, J. Nagata, and T. Mizuno, J. Agr. Chem. Soc. Japan, 27, 234 (1953); Chem. Abs., 49, 4802a (1955).
53. E. Mizuno and K. Hayashi, Nippon Nogei Kagaku Kaishi, 31, 138, 142 (1957); Chem. Abs., 52, 18682d (1958).
54. B. N. Stepanenko, O. N. Ponomareva, E. M. Afanas'eva, and R. A. Baksova, Dokl. Akad. Nauk SSSR, 111, 652 (1956).
55. B. N. Stepanenko, E. M. Afanas'eva, and R. A. Baksova, Biokhimiya, 23, 712 (1958).
56. B. N. Stepanenko and E. M. Afanas'eva, "Uglevody i Uglovodnyi Obmen" (Carbohydrates and Carbohydrate Exchange), Izd. Akad. Nauk SSSR, 1959, p. 203.
57. B. N. Stepanenko, Izv. Akad. Nauk SSSR, Ser. Biol., No. 2, 294 (1960).
58. P. Andrews, L. Hough, and I. K. Jones, J. Chem. Soc., 1186 (1953).
59. K. Hayashi and P. Mizuno, J. Agr. Chem. Soc. Japan, 26, 569 (1952); Chem. Abs., 49, 4803f (1955).
60. O. Moe, S. Miller, and M. Backly, J. Amer. Chem. Soc., 74, 1325 (1952).
61. O. Moe, U. S. P. 2 599 771; Chem. Abs., 46, 9876g (1952).
62. O. Moe, U. S. P. 2 650 917; Chem. Abs., 48, 394f (1954).
63. T. Hata, J. Ono, and K. Maeda, J. Chem. Soc. Japan, 54, 532 (1951).
64. E. Cabib and L. Leloir, J. Biol. Chem., 206, 779 (1954).
65. T. Asai and H. Saito, J. Agr. Chem. Soc. Japan, 25, 431 (1952); Chem. Abs., 47, 64776 (1953).
66. N. Jnoue, J. Ferm. Technol., 25, 145 (1947); Chem. Abs., 47, 1251 (1953).
67. M. Heidelberger, J. Amer. Chem. Soc., 77, 4308 (1955).
68. L. Stoloff, Adv. Carbohydrate Chem., 13, 265 (1958).
69. R. Hegnauer, Planta Med., 4, 198 (1956).
70. G. Elverum and P. Ramstad, U. S. P. 2 891 050 (June 1959); Chem. Abs., 55, 18524a (1959).
71. M. Hefti, Ital. P. 498 739 (1954); Chem. Abs., 51, 8459d (1957).
72. A. M. Goldstein, U. S. P. 2 868 664 (Jan. 13th, 1959); Chem. Abs., 53, 6618 (1959).
73. C. Anker, U. S. P. 2 834 774; Chem. Abs., 52, 14206b (1958).
74. H. Jakobs, J. Sci. Research, Indonesia, 1, 129 (1952).
75. I. Nordman and A. Kärna, Paperi ja Puu, 40, 45, 54 (1958); Chem. Abs., 52, 19135g (1958).
76. A. Goldstein, Tappi, 40, 9, 180A–182A (1957).
77. M. Cushing, Tappi, 41, No. 7, 155A (1958).
78. D. Bandel, U. S. P. 2 769 734; Chem. Abs., 51, 3941c (1957).
79. M. Samfield, B. Brock, and E. Locklair, U. S. P. 2 708 175 (1955); Chem. Abs., 49, 11248f (1955).
80. H. Hutchins and R. Singiser, J. Amer. Pharm. Assoc., Pract. Pharm. Edn., 16, 226 (1955).
81. Ch. Becker, Am. Profess. Pharmacist, 20, 939, 987 (1954).
82. C. Griffiths, Food, 21, 58 (1952); Chem. Abs., 46, 3181d, (1952).
83. T. Strange, J. Assoc. Offic. Agric. Chemists, 40, 482 (1957).
84. E. Letzig, Deut. Lebensm.-Rundschau, 51, 41 (1955).

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THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

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INTRODUCTION

The study of the action of different forms of radiation on aqueous solutions is important chiefly because of the marked similarity in the behaviour of the primary products of the radiolysis of aqueous solutions and biological systems. On practical application is the construction of chemical dosimeters, which are not only air-equivalent but also simulate tissue behaviour. Moreover, the present development of atomic energy makes it important to take account of processes initiated by radiation and to examine possible methods of carrying out various redox reactions in inorganic and organic synthesis in aqueous solution. It is important to make maximum use of the energy absorbed when carrying out these processes.

These more general problems require the study of the nature of the primary products, the ways in which the energy absorbed by the solution can be transferred, and the mechanism of the reaction of the primary products with one another and with dissolved substances.

Although the effect of ionising radiation in aqueous solutions has been known for more than 50 years, there is as yet no single theory of the radiolysis of aqueous solutions. In this paper we have tried to show the main directions of development of the radiation chemistry of aqueous solutions, to examine modern theories of the mechanism of radiolytic changes, and to present what is in our opinion some of the most interesting effects of radiolytic reactions. We have taken into consideration the fact that the experimental material on the radiolysis of aqueous solutions has been presented fairly completely in a number of reviews on radiation chemistry[1-17].