972. *Polysaccharides of Soy-beans. Part I. Galactomannans from the Hulls.*

By G. O. Aspinall and J. N. C. Whyte.

Two galactomannan fractions have been isolated by extraction of soy-bean hulls with water at room temperature and at 60°. The two polysaccharide fractions, which contain D-galactose and D-mannose residues in the proportions of 1 : 1·4 and 1 : 2·35, have been shown by methylation and partial hydrolysis to possess similar structures in which linear chains of 1,4-linked β-D-mannopyranose residues carry at intervals side-chains of single α-D-galactopyranose residues attached by 1→6 linkages.

Whistler and Saarnio [1] have shown that soy-bean hulls contain a galactomannan which may be isolated by extraction with cold water. The isolation of 2,3,4,6-tetra-*O*-methyl-D-galactose, and 2,3,6-tri- and 2,3-di-*O*-methyl-D-mannose on hydrolysis of the methylated polysaccharide suggested that this galactomannan possessed a structure similar to those of guaran and other galactomannans from the seeds of leguminous plants.[2] We report herein a more detailed examination of galactomannan fractions from soy-bean hulls, as part of an extensive investigation of soy-bean polysaccharides.

The hulls were extracted with water at room temperature to give a mixture of polysaccharides. Galactomannan I was isolated pure after precipitation of the contaminating acidic polysaccharide as its insoluble copper salt. A second polysaccharide, galactomannan II, was isolated in a similar manner by subsequent extraction of the hulls with water at 60°. Hydrolysis of the two polysaccharide samples gave galactose and mannose in the proportions of 1 : 1·4 and 1 : 2·35, respectively. Traces of other sugars were shown to arise from slight contamination with acidic polysaccharides since pure galactomannans could be obtained after chromatography on diethylaminoethylcellulose.

Hydrolysis of methylated galactomannan I gave, as the main products, 2,3,4,6-tetra-*O*-methyl-D-galactose and 2,3,6-tri- and 2,3-di-*O*-methyl-D-mannose, with small amounts of 2,3,4,6-tetra-*O*-methyl-D-mannose and 2,3,6- and 2,4,6-tri-*O*-methyl-D-galactose, and traces of other sugars which were probably of little structural significance. Tetra-*O*-methyl-D-mannose probably arose from end groups of the main chain, but it is not possible to ascribe definite structural significance to the trimethyl ethers of D-galactose. These tri-ethers could have arisen from a small proportion of non-terminal galactose residues, but their origin either in demethylation during hydrolysis of the methylated polysaccharide or in hydrolysis of minor polysaccharide contaminants is equally possible. Methylated galactomannan II was not examined in detail, but gas chromatography of the methyl glycosides formed on methanolysis showed the main cleavage products to be qualitatively similar to those from methylated galactomannan I. Quantitative paper chromatography of the main hydrolysis products of the two methylated galactomannans showed the formation of tetra-*O*-methylgalactose and tri- and di-*O*-methylmannose in the molar ratios of 2·3 : 1·0 : 2·1 and 1·0 : 1·83 : 1·0 severally. Methylated galactomannan I contained galactose and mannose residues in the same proportion as in the parent polysaccharide. Methylated galactomannan II, however, contained a lower proportion of galactose residues (as methylated derivative) than in the parent polysaccharide, and it is probable that some inadvertent fractionation had occurred during the formation of the methylated derivative so that it was not quantitatively representative of the starting material.

Partial hydrolysis of the galactomannans was effected by graded acetolysis followed by deacetylation of the derived sugar acetates. The two galactomannans furnished chromatographically similar mixtures of mono- and oligo-saccharides, which were combined

[1] Whistler and Saarnio, *J. Amer. Chem. Soc.*, 1957, **79**, 6055.
[2] Smith and Montgomery, "Chemistry of Plant Gums and Mucilages," Reinhold Publ. Corp., New York, 1959.

and fractionated by chromatography on charcoal–Celite followed, as required, by chromatography on cellulose. The following crystalline oligosaccharides were characterised as partial hydrolysis products: 6-*O*-α-D-galactopyranosyl-D-mannose, 4-*O*-β-D-mannopyranosyl-D-mannose, and the polymer-homologous mannotriose, mannotetraose, and mannopentaose. Although *O*-α-D-galactopyranosyl-(1→6)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose was not isolated as the crystalline trisaccharide, the sugar was recognised by paper chromatography of 6-*O*-α-galacto- and 4-*O*-β-manno-pyranosylmannose as partial hydrolysis products and by gas chromatography of methyl glycosides of 2,3,4,6-tetra-*O*-methylgalactose and 2,3,4- and 2,3,6-tri-*O*-methylmannose (cleavage products of the methylated derivative). In addition, minor amounts of two series of oligosaccharides were formed as artefacts. 4-*O*-β-Mannopyranosylglucose and *O*-β-mannopyranosyl-(1→4)-*O*-β-mannopyranosyl(1→4)-glucose were probably formed by epimerisation during the deacetylation of the sugar acetates since glucose was not detected as a constituent of the polysaccharides. 4-*O*-α-D-Mannopyranosyl-D-mannose and *O*-α-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose were probably formed from the acid-catalysed anomerisation of β-D-mannopyranose residues during acetolysis as shown previously in control experiments.[3]

These experiments establish the structures of the two galactomannan fractions and show that the two polysaccharides contain linear chains of 1,4-linked β-D-mannopyranose residues to which different proportions of α-D-galactopyranose residues are attached as single unit side-chains by 1→6 linkages. It is not possible, on the present evidence, to state whether the two galactomannans arise from the arbitrary fractionation of a continuous spectrum of closely related molecular species which contain varying proportions of galactose residues, or whether the two fractions result from a definite discontinuity in the proportions of the two sugar units in structurally similar polysaccharides. It is noteworthy that subsequent extraction of soy-bean hulls with alkaline borate solutions furnishes a small quantity of a further galactomannan which contains a markedly lower proportion of galactose residues.[4]

Experimental

Paper chromatography was carried out with the following solvent systems (v/v): (A) ethyl acetate–pyridine–water (10 : 4 : 3); (B) ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4); (C) butan-1-ol–ethanol–water (4 : 1 : 1); (D) butan-2-one–light petroleum (b. p. 100—120°) (9 : 1, half saturated with water); (E) butan-1-ol–ethanol–water (1 : 1 : 1). R_G values of methylated sugars refer to rates of movement relative to 2,3,4,6-tetra-*O*-methyl-D-glucose in solvent C. Demethylations of methylated sugars were performed with boron trichloride.[5] Paper ionophoresis was in borate buffer at pH 10. Small-scale methylations of oligosaccharides were carried out by the procedure of Kuhn, Trischmann, and Löw.[6] Unless otherwise stated, optical rotations were observed for water solutions at *ca.* 18°.

Gas–liquid chromatography of methylated and partially methylated methyl glycosides was carried out on columns of (*a*) 15% by weight of tetramethylene succinate polyester on Celite at 175°; (*b*) 10% by weight of polyphenyl ether [*m*-bis-(*m*-phenoxyphenoxy)benzene] on Celite at 200°.[7]

Isolation of Galactomannans I and II.—Soy-beans ("Lindarin" variety) were soaked in acetone for 24 hr., crushed gently to rupture the hulls, and separated into hulls, cotyledons, and hypocotyls. The hulls were extracted (Soxhlet) with, successively, acetone, light petroleum (b. p. 60—80°), and ethanol–water (4 : 1) to remove lipids, colouring matter, and soluble sugars. The defatted hulls (787 g.) were exhaustively extracted with water (6 × 6 l.) at room temperature, and the filtered solutions were concentrated to one-half of their original volume and adjusted to pH 4·5 in an attempt to precipitate protein. A small precipitate (2·2 g.) was

[3] Aspinall, Begbie, and McKay, *J.*, 1962, 214.
[4] Aspinall and Morrison, unpublished results.
[5] Bonner, Bourne, and McNally, *J.*, 1960, 2929.
[6] Kuhn, Trischmann, and Löw, *Angew. Chem.*, 1955, **67**, 32.
[7] Aspinall, *J.*, 1963, 1676.

separated and the solution was further concentrated and poured into ethanol to give polysaccharide mixture A (60 g.). Hydrolysis of a sample of the crude polysaccharide gave galacturonic acic galactose, mannose, arabinose, xylose, and traces of fucose, rhamnose, and two methylated sugars (probably 2-*O*-methylxylose and 2-*O*-methylfucose). 7% Aqueous cupric acetate (600 ml.) was added to the polysaccharide mixture (59 g.) in water (6 l.), and the insoluble copper complex A was removed at the centrifuge. On addition of ethanol (2 vol.), copper complex B separated. Copper complex A was decomposed by treatment with ethanol containing 1% of hydrogen chloride and furnished a polysaccharide (11 g.), $[\alpha]_D$ +126° (*c* 1·6), which gave on hydrolysis galacturonic acid, galactose, mannose, arabinose, xylose, and traces of fucose, rhamnose, and two methylated sugars. Copper complex B similarly afforded galactomannan I (11 g.), $[\alpha]_D$ +68° (*c* 1·0), hydrolysis of which gave galactose and mannose in the ratio of 1 : 1·4, together with a trace of arabinose.

Further extraction of soy-bean hulls with water (6 × 6 l.) at 60° furnished a similar polysaccharide mixture (45 g.), and a sample (183 mg.) of the polysaccharide mixture was chromatographed on diethylaminoethylcellulose (phosphate form).[8] The column was eluted successively with 0·025, 0·05, 0·10, and 0·25M-sodium dihydrogen phosphate at pH 6, and then with a gradient of 0·01—0·5N-sodium hydroxide. Galactomannan (37 mg.), $[\alpha]_D$ +30° (*c* 1·0), was eluted with 0·025M-buffer and gave only galactose and mannose on hydrolysis. A second polysaccharide fraction (197 mg.), which was probably contaminated with cellulosic material, was eluted with sodium hydroxide. Hydrolysis gave, in addition to glucose, galacturonic acid, galactose, mannose, arabinose, xylose, fucose, rhamnose, and traces of two methylated sugars. The polysaccharide mixture (44 g.) was fractionated as described previously *via* copper complexes, to give (*a*) a complex acidic polysaccharide (14 g.), $[\alpha]_D$ +75° (*c* 1·4), and (*b*) galactomannan II (5 g.), $[\alpha]_D$ +26·5° (*c* 1·0), hydrolysis of which gave galactose and mannose in the ratio of 1 : 2·35, together with traces of arabinose and xylose. Galactomannan II (350 mg.) was chromatographed on diethylaminoethylcellulose (phosphate form) with phosphate buffers as described previously and then with 0·5M-sodium chloride. Galactomannan IIa (285 mg.), $[\alpha]_D$ +22° (*c* 1·0) was eluted with 0·025M-buffer and gave only galactose and mannose on hydrolysis. A small amount (5 mg.) of a complex acidic polysaccharide was eluted with sodium chloride solution.

Preparation and Hydrolysis of Methylated Galactomannan I.—Galactomannan I (2·35 g.) was methylated successively with methyl sulphate–sodium hydroxide and methyl iodide–silver oxide, to give methylated polysaccharide (1·84 g.), the major part (1·75 g.) of which was fractionated by dissolution in boiling mixtures of chloroform–light petroleum (b. p. 60—80°). The main fraction (1·6 g.) was soluble in chloroform–light petroleum (1 : 4) and after reprecipitation furnished methylated galactomannan I (1·5 g.), $[\alpha]_D$ +56° (*c* 1·0 in $CHCl_3$) (Found: OMe, 44·3%).

Methylated galactomannan I (1·36 g.) was dispersed in 72% sulphuric acid (9 ml.) at 0° for 30 min. The resulting solution was diluted with water to 216 ml., kept overnight at room temperature, and heated at 60° for 18 hr. and on the boiling-water bath for 3 hr. The cooled solution was neutralised by passage through a column of Duolite resin A4(OH) and concentrated to a syrup (1·32 g.), which was separated on cellulose (60 × 3 cm.), light petroleum (b. p. 100—120°)–butan-1-ol (7 : 3, later 1 : 1), saturated with water, and butan-1-ol, half saturated with water, being used as eluants to give ten fractions. The Table summarises the results of preliminary examination of the various fractions.

Characterisation of Methylated Sugars.—Fraction 2 was characterised as 2,3,4,6-tetra-*O*-methyl-D-galactose by conversion into the aniline derivative, m. p. and mixed m. p. 197—198°. Fraction 3 was characterised as 2,3,6-tri-*O*-methyl-D-mannose by conversion into the 1,4-di-*p*-nitrobenzoate, m. p. and mixed m. p. 187—188°. The major component of fractions 4 and 5 was identified as 2,3,6-tri-*O*-methyl-D-galactose by conversion into 2,3,6-tri-*O*-methyl-D-galactonolactone, m. p. and mixed m. p. 97—98°. The major component of fraction 7 was characterised as 2,4,6-tri-*O*-methyl-D-galactose by conversion into the aniline derivative, m. p. and mixed m. p. 174—177°. Fraction 9 was characterised as 2,3-di-*O*-methyl-D-mannose by conversion into 2,3-di-*O*-methyl-D-mannonophenylhydrazide, m. p. and mixed m. p. 159—160°.

Preparation of Other Methylated Galactomannan Samples and Examination of Cleavage Products.—Methylation of galactomannan II (0·54 g.), as described for galactomannan I,

[8] Neukom, Deuel, Heri, and Kundig, *Helv. Chim. Acta*, 1960, **43**, 67.

Analysis, by paper chromatography,* of hydrolysate of methylated galactomannan I.

Fraction	Wt. (mg.)	$[\alpha]_D$	R_G		Sugars given on demethyln.	Other evidence †
1	15	+2·5°	1·08	Me_4-mannose 2,3,5-Me_3-arabinose (*t*)	Mannose Arabinose (*t*)	GLC, D
2	392	+101	0·95	Me_4-galactose	Galactose	GLC, D
3	286	−6·0	0·85	2,3,6-Me_3-mannose	Mannose	GLC
4	24	+81	0·83	2,3,6-Me_3-mannose (*t*) 2,3,6-Me_3-galactose	Mannose (*t*) Galactose	GLC
5	13	+82	0·83	2,36-Me_3-galactose	Galactose	GLC
6	7		0·83 0·79	2,3,6-Me_3-galactose 2,4,6-Me_3-galactose (*t*) 2,3-Me_2-arabinose	Galactose Arabinose (*t*)	GLC
7	8		0·83 0·78	2,3,6-Me_3-galactose (*t*) 2,4,6-Me_3-galactose 2,3-Me_2-arabinose (*t*)	Galactose Arabinose (*t*)	GLC
8	10		0·77	2,3,4-Me_3-galactose 2,3-Me_2-arabinose (*t*)	Galactose Arabinose (*t*)	GLC
9	441	−16	0·68	2,3-Me_2-mannose	Mannose	GLC
10	20		0·62 0·56 0·29	(?) Me_2-galactose (?) Me_2-mannose (?) Me-mannose	Galactose Mannose	

* *t* = trace. † D = Paper chromatography in solvent D. GLC = gas chromatography of the methyl glycosides.

afforded methylated galactomannan II (0·26 g.), $[\alpha]_D$ +12° (*c* 1·0 in $CHCl_3$) (Found: OMe, 44·0%). Similarly, galactomannan II*a* (from chromatography on diethylaminoethylcellulose) (0·07 g.) furnished methylated galactomannan II*a* (0·03 g.), $[\alpha]_D$ +12° (*c* 1·0 in $CHCl_3$) (Found: OMe, 44·2%). Samples of methylated galactomannans II and II*a* were heated with methanolic hydrogen chloride, and gas chromatography of the products on columns *a* and *b*, showed the presence of components having the retention times of methyl glycosides of 2,3,4,6-tetra-*O*-methyl-D-galactose, 2,3,6-tri- and 2,3-di-*O*-methyl-D-mannose, and, as a minor component, 2,3,4,6-tetra-*O*-methyl-D-mannose.

The hydrolysis products from methylated galactomannans I and II were separated chromatographically in solvent C and quantitative estimation [9] showed the presence of tetra-*O*-methylgalactose and tri- and di-*O*-methylmannose in the molar ratios of 2·3 : 1·0 : 2·1 and 1·0 : 1·83 : 1·0, respectively.

Acetolysis of Galactomannans I and II. Deacetylation and Characterisation of Oligosaccharides.—Galactomannan I (5·08 g.) was added slowly with stirring to a mixture of acetic anhydride (50 ml.), acetic acid (50 ml.), and concentrated sulphuric acid (5 ml.), and the mixture was kept at room temperature for 72 hr. The resulting solution was poured into ice–water (300 ml.), and sodium hydrogen carbonate was added gradually to pH 4—5. The precipitated sugar acetates were separated and dissolved in chloroform (100 ml.), and the aqueous solution was extracted with chloroform (4 × 100 ml.). The combined chloroform solutions were washed with sodium hydrogen carbonate solution, dried, and concentrated to a syrup (*ca.* 8 g.). 0·5N-Barium methoxide in methanol (50 ml.) was added to the syrup acetates in chloroform (10 ml.) and methanol (20 ml.), and the mixture was kept at 0° for 24 hr. The mixture was poured into water (200 ml.), barium ions were precipitated by neutralisation with dilute sulphuric acid to pH 7, and the filtrate was passed through columns of Amberlite IR-120(H) and Duolite A4(OH) resins and concentrated to a syrup (3·18 g.). In a similar manner galactomannan II (2·3 g.) furnished a syrupy mixture (1·68 g.) of sugars. Chromatography of the two mixtures of sugar in solvents A and B indicated the presence of the same components including mannose, galactose, mannobiose, mannotriose, galactosylmannose, and higher oligosaccharides. The combined mixtures (4·77 g.) in water were added to a column of charcoal–Celite (300 g.; 1 : 1). Elution with water yielded a mixture (1·74 g.) of monosaccharides (mannose, galactose, and traces of arabinose and xylose) and a trace of mannobiose which were not examined further. Elution with water containing increasing proportions of ethanol gave twelve oligosaccharides, some of which were re-fractionated by chromatography on filter sheets, with appropriate solvents.

Oligosaccharide 1. The sugar (376 mg.; eluted with water containing 1·0—5·0% of ethanol),

[9] Chanda, Hirst, Jones, and Percival, *J.*, 1950, 1289.

$R_{glucose}$ 0·50 in solvent A, M_G 0·54, recrystallised from ethanol containing a trace of water, had m. p. and mixed m. p. 205°, $[\alpha]_D$ −7·5° (equil.) (*c* 5·1), and gave an *X*-ray powder photograph identical with that given by 4-*O*-β-D-mannopyranosyl-D-mannose.

Oligosaccharide 2. The sugar (8 mg.; eluted with water containing 1·0—5·0% of ethanol), $R_{glucose}$ 0·66 in solvent A, M_G 0·57, $[\alpha]_D$ +66° (*c* 0·68), gave only mannose on hydrolysis and was chromatographically and ionophoretically indistinguishable from 4-*O*-α-D-mannopyranosyl-D-mannose from ivory-nut mannan.[10] The methanolysis products from the methylated disaccharide were examined by gas chromatography, and the main components had the retention times of methyl glycosides of 2,3,4,6-tetra- and 2,3,6-tri-*O*-methyl-D-mannose.

Oligosaccharide 3. The sugar (40 mg.; eluted with water containing 1·0—5·0% of ethanol), $R_{glucose}$ 0·42 in solvent A, M_G 0·65, was recrystallised from ethanol–water to give 6-*O*-α-D-galactopyranosyl-D-mannose which was identified by m. p. and mixed m. p. 201°, $[\alpha]_D$ +122° (equil.) (*c* 1·0), and by *X*-ray powder photograph.

Oligosaccharide 4. The sugar (1 mg.; eluted with water containing 1·0—5·0% of ethanol), $R_{glucose}$ 0·35 in solvent A, M_G 0·36, gave mannose and glucose on hydrolysis, and was chromatographically and ionophoretically indistinguishable from 4-*O*-β-D-mannopyranosyl-D-glucose.

Oligosaccharide 5. The sugar (2 mg.; eluted with water containing 1·0—5·0% of ethanol), $R_{glucose}$ 0·25 in solvent A, M_G 0·80, gave galactose only on hydrolysis, and was chromatographically and ionophoretically indistinguishable from 6-*O*-β-D-galactopyranosyl-D-galactose.

Oligosaccharide 6. The sugar (254 mg.; eluted with water containing 5·0—7·5% of ethanol), $R_{glucose}$ 0·17 in solvent A, M_G 0·50, was recrystallised from ethanol–water to give *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose trihydrate which was identified by m. p. (sealed tube) 131—132°, m. p. and mixed m. p. 166—168° (slow heating), $[\alpha]_D$ −15°→−20° (equil.) (*c* 1·1), and by *X*-ray powder photograph.

Oligosaccharide 7. The sugar (12 mg.; eluted with water containing 5·0—7·5% of ethanol), $R_{glucose}$ 0·22 in solvent A, M_G 0·60, was recrystallised from ethanol–water to give *O*-α-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-mannose which was identified by m. p. and mixed m. p. (with sample from ivory-nut mannan) [10] 224°, $[\alpha]_D$ +41° (equil.) (*c* 1·2), and by *X*-ray powder photograph.

Oligosaccharide 8. The sugar (17 mg.; eluted with water containing 5·0—7·5% of ethanol), $R_{glucose}$ 0·16 in solvent A, M_G 0·48, $[\alpha]_D$ +31° (*c* 0·9), gave on hydrolysis galactose and mannose in the approximate proportions of 1 : 2. Partial hydrolysis furnished galactose, mannose, mannobiose, and 6-*O*-α-galactopyranosylmannose, whereas partial hydrolysis of the derived glycitol (borohydride reduction) gave 6-*O*-α-galactopyranosylmannose as the sole reducing disaccharide. The methanolysis products from the methylated trisaccharide were examined by gas chromatography and the main components had the retention times of methyl glycosides of 2,3,4,6-tetra-*O*-methyl-D-galactose, and 2,3,4,- and 2,3,6-tri-*O*-methyl-D-mannose.

Oligosaccharide 9. The sugar (5 mg.; eluted with water containing 5·0—7·5% of ethanol), $R_{glucose}$ 0·12 in solvent A, M_G 0·38, $[\alpha]_D$ −10° (*c* 0·4), gave mannose and glucose on hydrolysis and was chromatographically and ionophoretically indistinguishable from *O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-mannopyranosyl-(1→4)-D-glucose. Partial acid hydrolysis yielded glucose, mannose, mannobiose, and 4-*O*-β-mannopyranosylglucose, whereas partial hydrolysis of the derived glycitol (borohydride reduction) gave mannobiose as the only reducing disaccharide.

Oligosaccharide 10. The sugar (20 mg.; eluted with water containing 7·5—12·5% of ethanol $R_{glucose}$ 0·32 in solvent E, M_G 0·47, was recrystallised from ethanol–water to give mannotetraose which was identified by m. p. and mixed m. p. (with sample from ivory-nut mannan) [10] 231—232°, $[\alpha]_D$ −30°→−28° (equil.) (*c* 1·5), and by *X*-ray powder photograph.

Oligosaccharide 11. The syrup (80 mg.; eluted with water containing 12·5—15·0% of ethanol), was chromatographically homogeneous ($R_{glucose}$ 0·41 in solvent E), but ionophoresis showed the presence of two components (M_G 0·47 and 0·53), the latter having the mobility of the mannotetraose containing one α-glycosidic linkage from ivory-nut mannan.[10] Partial acid hydrolysis afforded galactose, mannose, 4-*O*-α- and 4-*O*-β-mannobiose, 6-*O*-α-galactopyranosylmannose, and higher oligosaccharides.

Oligosaccharide 12. The sugar (15 mg.; eluted with water containing 12·5—15·0% of ethanol), $R_{glucose}$ 0·04 in solvent E, M_G 0·41, crystallised from ethanol–water and had $[\alpha]_D$ −30°

[10] Aspinall, Kessler, and Rashbrook, *J.*, 1958, 215.

(*c* 0·98); no m. p. (>280°) could be recorded. The *X*-ray powder photograph was identical with that of mannopentaose from ivory-nut mannan.[10]

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