Carbohydrate Research, 54 (1977) 115–124

THE STRUCTURE OF BAEL (*Aegle marmelos*) GUM*

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(Received October 2nd, 1976, accepted for publication November 2nd, 1976)

ABSTRACT

Purified, bael-gum polysaccharide contains D-galactose (71%), L-arabinose (12.5%), L-rhamnose (6.5%), and D-galacturonic acid (7%). Hydrolysis of one mole of the fully methylated polysaccharide gave (*a*) from the neutral part, 2,3,4-tri-*O*-methyl-L-rhamnose (2 moles), 2,3,5-tri-*O*-methyl-L-arabinose (4 moles), 2,3,4,6-tetra-*O*-methyl-D-galactose (8 moles), 3,4-di-*O*-methyl-L-rhamnose (2 moles), 2,5-di-*O*-methyl-L-arabinose (1 mole), 2,4,6-tri-*O*-methyl-D-galactose (10 moles), 2,3-di-*O*-methyl-L-arabinose (1 mole), 2,4-di-*O*-methyl-D-galactose (14 moles), and 2-*O*-methyl-D-galactose (2 moles), and (*b*) from the acidic part, 2,3,4-tri-*O*-methyl-D-galacturonic acid (1 mole), 2,4,6-tri-*O*-methyl-3-*O*-(2,3,4-tri-*O*-methyl-D-galactopyranosyluronic acid)-D-galactose (2.6 moles), and 2,4,6-tri-*O*-methyl-3-*O*-[2,4,6-tri-*O*-methyl-3-*O*-(2,3,4-tri-*O*-methyl-D-galactopyranosyluronic acid)-D-galactopyranosyl]-D-galactose (1 mole). Mild hydrolysis of the whole gum yielded oligosaccharides from which 3-*O*-β-D-galactopyranosyl-L-arabinose, 5-*O*-β-D-galactopyranosyl-L-arabinose, 3-*O*-β-D-galactopyranosyl-D-galactose, and 6-*O*-β-D-galactopyranosyl-D-galactose could be isolated and characterized. The results of methylation, periodate oxidation, Smith degradation, Barry degradation, and graded hydrolysis studies were employed for the elucidation of the structure of the whole gum.

INTRODUCTION

In previous communications[1,2], structural studies on the degraded bael gum obtained by mild treatment of the whole gum with oxalic acid were reported.

The purified gum from bael fruit (*Aegle marmelos*) has $[\alpha]_D$ +84° (in water), and contains galactose (71%), arabinose (12.5%), rhamnose (6.5%), and galacturonic acid (7%). The homogeneity of bael gum was confirmed by paper electrophoresis. Investigations on elucidation of the structure of the average repeating-unit of the polysaccharide present in bael gum are reported here.

*Structural Investigations on Bael (*Aegle marmelos*) Gum. Part III, for Parts I and II, see refs. 1 and 2, respectively.

RESULTS AND DISCUSSION

The gum was methylated, first by the Hakomori method[3] and then by Purdie's method[4], to obtain a permethylated product, $[\alpha]_D^{30}$ −40° (in chloroform), this was methanolyzed with methanolic hydrogen chloride, and the methyl esters were saponified with barium hydroxide solution After neutralization of the excess of base with carbon dioxide, the acidic methyl sugars were adsorbed on a column of Dowex-1 X-4 (HCO_3^-) resin The eluate and the washings from this column contained the methyl glycosides of neutral, methylated sugars, these were combined, and evaporated to a syrup which was hydrolyzed with aqueous hydrochloric acid The hydrolyzate, after the usual treatment, was examined chromatographically Nine spots were detected on a paper chromatogram The mixture was resolved on Whatman No 3 MM filter paper into its components, which were characterized, and their mole ratios determined 2,3,4,6-tetra-*O*-methyl-D-galactose (8 moles), 2,4,6-tri-*O*-methyl-D-galactose (10 moles), 2,4-di-*O*-methyl-D-galactose (14 moles), 2-*O*-methyl-D-galactose (2 moles), 2,3,4-tri-*O*-methyl-L-rhamnose (2 moles), 3,4-di-*O*-methyl-L-rhamnose (2 moles), 2,3,5-tri-*O*-methyl-L-arabinose (4 moles), 2,3-di-*O*-methyl-L-arabinose (1 mole), and 2,5-di-*O*-methyl-L-arabinose (1 mole)

The acid fraction was displaced from the anion-exchange resin and, after the usual treatment, was examined on paper chromatograms Three spots were detected The individual, methylated acid sugars were isolated, characterized, and their molar ratios determined 2,3,4-tri-*O*-methyl-D-galacturonic acid (1 mole), 2,4,6-tri-*O*-methyl-3-*O*-(2,3,4-tri-*O*-methyl-D-galactopyranosyluronic acid)-D-galactose (2 6 moles), and 2,4,6-tri-*O*-methyl-3-*O*-[2,4,6-tri-*O*-methyl-3-*O*-(2,3,4-tri-*O*-methyl-D-galactopyranosyluronic acid)-D-galactopyranosyl]-D-galactose (1 mole)

In the bael gum, the proportion of galacturonic acid accounts for 7 0%, but the acid fraction (375 mg) obtained from the hydrolyzate of the methylated, whole gum is ~13% of the total mixture (2 87 g) This was to be expected, as the acid fraction contained mainly aldobiouronic acid, and the monouronic and aldotriouronic acids are in the same proportion

Isolation of only 2,3,4-tri-*O*-methyl-D-galacturonic acid (and no di- or mono-*O*-methylgalacturonic acid) from the hydrolyzate indicated that all the galacturonic acid residues present in the molecule occur as nonreducing end-units, and that there are none in the interior of the molecule Isolation and characterization of the methyl aldobio- and aldotrio-uronic acids mentioned shows that these galacturonic acid residues are joined to the adjacent galactose moieties at O-3 It is possible that these galacturonic acid-containing branches may be three units long, or that they may contain even more units

Two methylated sugars were isolated from the hydrolyzate of the methylated, whole gum and characterized They were 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3,5-tri-*O*-methyl-L-arabinose These residues are obviously present as nonreducing end-units in the methylated polysaccharide molecule, as they appeared as tri-*O*-methyl-rhamnose and tri-*O*-methylarabinose The corresponding, unmethylated, acid-labile

residues are removed from the whole gum during the preparation of degraded gum, the loss of arabinose during this process is much more than that of rhamnose, and, correspondingly, the proportion of tri-*O*-methyl-L-arabinose is much greater than that of the tri-*O*-methyl-L-arabinose in the hydrolyzate of methylated, degraded gum

The molar proportions of tetra-, tri-, and di-*O*-methyl-D-galactose in the hydrolyzates of methylated, whole gum and methylated, degraded gum differed, as shown in Table I This shows that the acid-labile rhamnose and arabinose residues in the molecule are linked to galactose residues only The molar proportion of

TABLE I

MOLAR PROPORTIONS OF DIFFERENT METHYLATED SUGARS CHARACTERIZED, PRESENT IN THE HYDROLYZATES OF METHYLATED, DEGRADED GUM AND METHYLATED, WHOLE GUM

Fraction No	*Methylated sugars*	*Mole proportions in methylated*	
		Degraded gum	*Whole gum*
1	2 3 4 6 tetra *O* methyl-D galactose	12	8
2	2 4 6 tri *O* methyl D-galactose	8	10
3	2,4-di-*O*-methyl D galactose	12	14
4	2-*O*-methyl-D-galactose	2	2
5	2,3,4-tri-*O*-methyl-L-rhamnose	—	2
6	3 4-di-*O*-methyl-L-rhamnose	2	2
7	2 3,5 tri-*O*-methyl L-arabinose	—	4
8	2,3-di-*O*-methyl-L-arabinose	1	1
9	2,5-di-*O*-methyl L-arabinose	1	1
10	2,3,4 tri-*O* methyl D-galacturonic acid	1	1
11	2 4 6-tri-*O* methyl-3-*O*-(2 3 4-tri-*O*-methyl-D-galactopyranosyluronic acid)-D galactose	2 5	2 6
12	2 4,6 tri-*O*-methyl-3-*O*-[2,4,6-tri-*O*-methyl 3-*O*-(2,3,4-tri *O*-methyl-D-galactopyranosyluronic acid)-D galactopyranosyl] D galactose	1	1

2-*O*-methyl-D-galactose is constant (*viz*., 2 moles) in the hydrolyzates of methylated, whole gum and methylated, degraded gum It was found that the molar proportions of the tetra-*O*-methyl-D-galactose changed from 12 to 8, those of the tri-*O*-methyl-D-galactose, from 8 to 10, and those of the di-*O*-methyl-D-galactose, from 12 to 14 A total of 6 molar proportions of the methylated sugars, *viz*., 2,3,5-tri-*O*-methyl-L-arabinose (4 moles) and 2,3,4-tri-*O*-methyl-L-rhamnose (2 moles), appeared in the hydrolyzate of 1 mole of the methylated, whole gum, these can be explained as indicating a loss of 4 moles of tetra-*O*-methyl-D-galactose and 2 moles of tri-*O*-methyl-D-galactose, with a gain of 4 moles of tri-*O*-methyl-D-galactose and 2 moles of di-*O*-methyl-D-galactose

Considering all these facts, and with knowledge of the structure of the average repeating-unit of the polysaccharide[2] of the degraded gum, it is possible to assign a structure to the average repeating-unit of the polysaccharide present in whole bael gum (see Fig 1) This structure identifies the linkages through which the different

sugars are linked to each other It is not, however, possible to assign the correct sequence of branches in the main chain of the molecule from these data

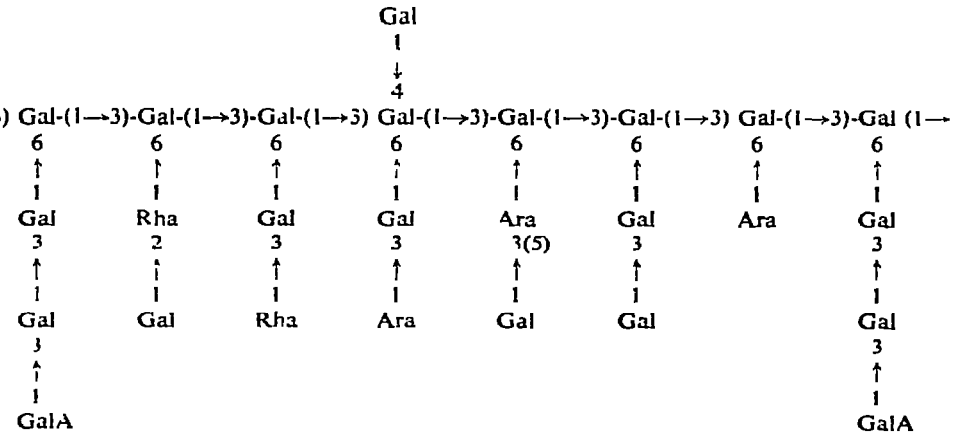

Fig 1 The average repeating-unit of the polysaccharide of the whole gum (where Gal represents a D-galactopyranosyl residue or group, GalA a D-galactopyranosyluronic acid group, Rha, an L-rhamnopyranosyl residue or group, and Ara an L arabinofuranosyl residue or group)

The results of periodate oxidation studies are in reasonable agreement with those to be expected from a polysaccharide having the average repeating-unit suggested The polysaccharide consumed 0 70 mole of periodate, liberating 0 30 mole of formic acid, per mole of hexose residue Theoretically, a polysaccharide with the structure shown would consume 0 67 mole of periodate, liberating 0 27 mole of formic acid, per mole of hexose residue

The periodate-oxidized polysaccharide was reduced with sodium borohydride and the product was isolated as usual The material contained 95% of galactose and 4% of arabinose A polysaccharide having the structure suggested would yield a product containing galactose and a small proportion of O-1- and O-3-linked arabinose after the first periodate oxidation and subsequent reduction When this material was subjected to a second Smith degradation, a product containing only galactose was obtained, this indicates that the backbone of the molecule consists of (1→3)-linked galactose residues only, from which branches originate Barry degradation[12] of the periodate-oxidized, whole gum yielded a material containing 94% of galactose and 4% of arabinose The results of all these studies support the structure advanced for the average repeating-unit of the bael-gum polysaccharide

The whole gum was subjected to graded hydrolysis with 0 05M sulfuric acid The neutral and acid fractions were separated and the oligosaccharides from each fraction were isolated and identified, they were 3-*O*-*β*-D-galactopyranosyl-L-arabinose 5-*O*-*β*-D-galactopyranosyl-L-arabinose, 3-*O*-*β*-D-galactopyranosyl-D-galactose, and 6-*O*-*β*-D-galactopyranosyl-D-galactose in the neutral fraction, and D-galacturonic acid, 3-*O*-(*β*-D-galactopyranosyluronic acid)-D-galactose, and 3-*O*-(*β*-D-galactopyranosyluronic acid)-3-*O*-*β*-D-galactopyranosyl-D-galactose in the acid fraction

All, except the (1→6)-linked galactobiose, had also been isolated from the products of graded hydrolysis of the degraded gum[1] The disaccharide obviously originated from the branching unit of the main chain The majority of the linkages are generally of the β-type, as is evident from the isolation and characterization of β-linked disaccharides

Graded-hydrolysis studies thus provide additional evidence for the linkages shown in the structure given for the average repeating-unit of the polysaccharide present in the whole gum isolated from bael fruit

EXPERIMENTAL

General — All specific rotations are equilibrium values Unless otherwise stated, all evaporations were conducted *in vacuo* at 30–40° Whatman No 1 MM filter paper was used for paper partition chromatography, and quantities up to 200 mg of sugar mixture were separated on Whatman No 3 MM paper The solvent mixtures (v/v) used for partition chromatography of sugars and their derivatives were (*A*) 18 3 1 4 ethyl acetate–acetic acid–formic acid–water, (*B*) upper layer of 4 1 5 1-butanol–acetic acid–water, (*C*) 5 5 1 3 ethyl acetate–pyridine–acetic acid–water, (*D*) 8 2 1 ethyl acetate–pyridine–water, (*E*) upper layer of 4 1 5 butanol–ethanol–water, and (*F*) 10 4 3 ethyl acetate–pyridine–water Spray reagents used were (*a*) aniline hydrogen oxalate, (*b*) benzidine periodate, and (*c*) alkaline silver nitrate The kinetics of periodate oxidation were studied spectrophotometrically[5,6], and the amount of formic acid liberated during the reaction was determined by titrating it with standard sodium hydroxide solution[7] The mole fraction of each methylated sugar was determined by the alkaline hypoiodite method[8]

Methylation of the whole gum — The purified bael gum (3 g) was methylated by the Hakomori method[3] The product was remethylated once by the Purdie method[4], to yield a fully methylated derivative showing no OH absorption band in its infrared spectrum, yield 3 3 g, $[\alpha]_D^{30}$ −40° (*c* 0 5, chloroform) Found OMe, 41 9%

Methanolysis of the methylated whole gum, and separation of the neutral and acidic components — A solution of the fully methylated gum (3 g) in 2 5% dry methanolic hydrogen chloride (150 ml) was boiled under reflux for 16 h, completion of methanolysis was ascertained by monitoring the optical rotations of the solution at regular intervals of time The solvent was removed under diminished pressure, and the resulting syrup was dissolved in water The solution was made neutral (Ag_2CO_3), the precipitate was centrifuged off, and the solution was evaporated to a syrup, this was heated with 2% barium hydroxide solution (90 ml) for 4 h at 80°, the solution was made neutral by passing in carbon dioxide gas, and the solid was centrifuged off The residue was washed several times with warm water, and the washings were combined with the main solution The resulting, clear solution was then passed successively through columns of Amberlite IR-120(H^+) and Dowex-1 X-4 (HCO_3^-) resin The Dowex column was washed thoroughly with water (3 liters), and the neutral solution and washings were combined, and concentrated to 30 ml

The mixture containing the methyl glycosides of the neutral sugars was hydrolyzed with 0 5M sulfuric acid on a boiling-water bath for 13 h The solution was cooled, made neutral ($BaCO_3$), the suspension centrifuged, and the supernatant liquor de-ionized and then evaporated to a syrup (2 5 g) Paper-chromatographic examination of the syrup revealed the presence of nine methylated sugars

The mixture was separated into its components on thick filter-papers, and each methylated sugar was obtained in a homogeneous state They were identified through their specific rotations, and by preparing crystalline products The results are given in Table II

Examination of the acidic components of the methylated whole gum — The mixture of methylated acid sugars was recovered from the Dowex column in the same way as for the methylated, degraded gum[2], to yield a syrup (370 mg) A part of the syrup (250 mg) was hydrolyzed by heating it with 0 25M sulfuric acid (25 ml) for 6 h on a boiling-water bath The hydrolyzate was made neutral with barium carbonate and the suspension filtered, the filtrate and washings were combined, passed through a column of Amberlite IR-120(H^+) resin, and evaporated to a syrup On paper-chromatographic examination (solvent *E*), the mixture gave three spots The mixture was separated on Whatman No 3 MM filter paper into its components, and each of them was isolated in homogeneous state The methyl ester methyl glycosides of the individual sugars were each reduced with lithium aluminum hydride in dry ether Hydrolysis, followed by the usual treatment, yielded neutral sugars which were characterized The results are given in Table III

Periodate oxidation of the whole gum — The whole gum was treated with 0 1M sodium metaperiodate in the dark at 0° Consumption of the oxidant and liberation of formic acid became constant within 10 h, corresponding to consumption of 0 70 mole of the oxidant and liberation of 0 30 mole of formic acid per molar equivalent of hexose residue

Smith degradation — The periodate-oxidized, whole gum (450 mg) was reduced with sodium borohydride[9] Part (5 mg) of the resulting material was hydrolyzed with 0 5M sulfuric acid for 18 h at 100° The hydrolyzate was made neutral ($BaCO_3$), and, after the usual treatment, was examined chromatographically (solvent *B*) Besides spots corresponding to lower polyhydric alcohols and aldehydes, galactose and arabinose (a trace) were detected The proportion of each sugar resistant to periodate oxidation was estimated to be galactose[10], 95%, and arabinose[11], 4%

A portion of the reduced, periodate-oxidized whole gum (18 mg) was dissolved in M sulfuric acid (10 ml), and the solution was kept for 2 days at room temperature The solution was made neutral ($BaCO_3$), and the suspension filtered The filtrate was concentrated to a small volume Chromatographic examination of this solution (solvents *C* and *D*) revealed the presence of galactose only The mixture was subjected to a second periodate oxidation at 3° in the dark Iodate and periodate ions were removed as the insoluble barium salts, and the resulting solution was concentrated to ~1 ml On complete hydrolysis of this material, followed by the usual treatments and

TABLE II

ANALYSIS OF THE NEUTRAL FRACTION OF THE METHYLATED WHOLE GUM

Fraction No	*Methylated sugars*	*Yield (mg)*	$[\alpha]_D^{30}$ *(degrees)*	*Derivative or crystalline product*		
				Name	$[\alpha]_D^{30}$ *(degrees)*	*M.p. (degrees)*
1	2,3,4-Tri-*O*-methyl L-rhamnose	70	+20 (lit [13] +22)	anilide		109 (lit [14] 111)
2	2,3,5-Tri-*O*-methyl L-arabinose	149	−39 (lit [15] −44)	amide	−17 (lit [16] +16)	134 (lit [16] 138)
3	2,3,4,6-Tetra-*O*-methyl D-galactose	295	+110 (lit [17] +104.5)	anilide	+41 (lit [18] +39)	186 (lit [19] 187)
4	3,4-Di-*O*-methyl L-rhamnose	69	+16 (lit [20] +18.6)	crystalline		95 (lit [20] 95–96)
5	2,5-Di-*O*-methyl L-arabinose	31	+80 (lit [21] +83)	amide	+41 (lit [21] +38)	130 (lit [21] 132)
6	2,4,6-Tri-*O*-methyl D-galactose	324	+87 (lit [22] +91.6)	anilide	+36 (lit [23] +38)	175 (lit [24] 178)
7	2,3-Di-*O*-methyl L-arabinose	33	+100 (lit [16] +101)	anilide		133 (lit [25] 138)
8	2,4-Di-*O*-methyl-D-galactose	495	+78 (lit [26] +85)	anilide		210 (lit [27] 216)
9	2-*O*-Methyl D-galactose	58	+82 (lit [28] +83)	anilide		161 (lit [28] 165)

TABLE III

ANALYSIS OF METHYLATED ACID SUGARS

Fraction No	*Methylated sugars*	*Yield (mg)*	*Neutral sugars obtained on reduction and hydrolysis*	$[\alpha]_D^{30}$ *(degrees)*	*Derivative*		
					Name	*M p (degrees)*	$[\alpha]_D^{30}$ *(degrees)*
1	2,3,4-Tri-*O* methyl-D galacturonic acid	30	2,3,4-tri *O*-methyl-D-galactose	+111 (lit [29] +114)	anilide	160 (lit [30] 160)	+37 (lit [26] +43)
2	2,4,6-Tri-*O* methyl-3-*O* (2,3,4-tri-*O*-methyl D-galactopyranosyluronic acid) D-galactose	150	(I) 2,4,6 tri *O*-methyl D-galactose	+87 (lit [22] +91.6)	anilide	175 (lit [24] 178)	+36 (lit [21] +38)
			(II) 2,3,4-tri-*O* methyl D galactose	Same as in acid fraction 1			
3	2,4,6-Tri-*O* methyl-3-*O* [2,4,6 tri-*O*-methyl 1-*O* (2,3,4-tri-*O*-methyl D-galactopyranosyluronic acid) D-galactopyranosyl]-D galactose	85	(I) 2,3,4-tri *O* methyl D galactose	same as in acid fraction 1			
			(II) 2,4,6-tri-*O*-methyl D-galactose	same as in acid fraction 2			

paper-chromatographic examination (solvents *C* and *D*), only a spot corresponding to galactose was detected

Barry degradation — A mixture of periodate-oxidized, whole gum (1 5 g), 9 1 l ethanol–water (130 ml), phenylhydrazine (5 ml), and acetic acid (5 ml) was heated for 1 5 h on a steam bath, concentrated to 5 ml, and extracted with ether Chromatographic examination of the ether layer did not show the presence of any sugar or its derivative, but the aqueous layer showed the presence of one spot at the origin

The aqueous layer was concentrated to 40 ml, and then heated for 8 h on a steam bath with benzoic acid (110 mg), ethanol (30 ml), and benzaldehyde (1 5 ml) The solution was evaporated to dryness, the product was taken up in water, and the solution was exhaustively extracted, first with chloroform and then with ether The extracts were combined, and the solvents were evaporated off The resulting syrup showed no spots corresponding to any sugars

The aqueous layer was concentrated, and examined by paper chromatography (solvents *D* and *B*), only one spot, at the origin, was detected A portion (300 mg) of the mixture was separated on thick filter-papers, and the portion of the papers at the origin was excised, and eluted with water The aqueous solution was concentrated to a small volume, and freeze-dried, to give a solid product (170 mg) that contained 94% of galactose and 4% of arabinose

Graded hydrolysis of bael gum — Bael gum (1 0 g) was subjected to hydrolysis with 0 05M sulfuric acid (100 ml) on a boiling-water bath for 40 h, the conditions being ascertained in a pilot experiment The neutral and acid fractions were separated as already described[1]

Characterization of 6-O-β-D-galactopyranosyl-D-galactose[32] — The neutral fraction (18 2 mg) had $[\alpha]_D^{30}$ +27° (*c* 0 5, water) [lit [31] +30° (*c* 0 15, water), lit [32] +35 2°] and R_{Gal} 0 20 in solvent *F* [lit [33] R_{Gal} 0 20, lit [32] R_{Gal} 0 16] The disaccharide was hydrolyzed with 0 5M sulfuric acid (1 ml), and after the usual treatment, the hydrolyzate was examined chromatographically using solvent *B* Only galactose was detected The molecular weight of the oligosaccharide was estimated, and found to be 336 (calculated for a disaccharide containing two hexose residues, 342) The disaccharide (6 mg) was converted into its methyl glycosides in the usual way, and the mixture was subjected to periodate oxidation at 3° in the dark One mole of the methyl glycosides of the disaccharide consumed 4 1 moles of the oxidant in 6 h In a separate experiment, it was found that 2 1 moles of formic acid were liberated from one mole of the disaccharide

Characterization of the other neutral and acidic sugars was achieved as described for the product of graded hydrolysis of the degraded gum[1]

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