Structural Studies of the Gum Jeol Polysaccharide

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Gum Jeol (Odina Wodier, Roxb) has been reported[1] to contain galactose, arabinose and galacturonic acid as constituent units. An aldobiuronic acid has also been reported. The constitution of the degraded gum obtained by the removal of the labile arabinose units has also been described.[2] This paper will report on the structural studies of the whole gum obtained by its repeated purification (equivalent weight 1150).

The supernatant liquid obtained during autohydrolysis was found by paper chromatography to contain a large proportion of L-arabinose, a trace of D-galactose, and an oligosaccharide having R_{gal} 1.36 in solvent G. The mixture was resolved on a cellulose column using solvent A, and the pure oligosaccharide obtained from fraction III was converted to a sirup. The molecular weight as determined by the alkaline hypoiodite method was 274, showing it to be a disaccharide of two pentose units. This was characterised as 3-*O*-L-arabofuranosyl-L-arabinose from hydrolysis and periodate oxidation studies (vide Experimental Section).

The purified gum was methylated[3-5] to a fully methylated polysaccharide showing no hydroxyl band in the infrared spectrum in the region of 3500~3600 cm^{-1}. It was soluble in chloroform and had $[\alpha]_D^{32}$ −37° (in chloroform). A portion of the methylated gum was subjected to methanolysis under conditions known to cause no cleavage of aldobiuronic acid. The methyl ester was hydrolysed with barium hydroxide,[6] and the acid fraction was separated by adsorbing it on Dowex 1-X4 (acetate-form) anion-exchange resin. The neutral glycosides were converted to a mixture of methyl sugars, which were separated on a cellulose column and identified through their crystalline derivatives (vide Experimental Section). These are shown in Table I.

The acid fraction was displaced from the resin column with 1 N sulphuric acid. Neutralisation, deionisation with Amberite IR-120(H) cation-exchange resin, and the evaporation of the resulting solution yielded a thick sirup with $[\alpha]_D^{32}$ +64° (in chloroform). This has been shown[2] to be 3-*O*-(2,3,4-tri-*O*-methyl-D-galactopyranosyluronic acid)-2,4-di-*O*-methyl-D-galactose, since, on reduction of the methyl ester methyl glycoside and subsequent hydrolysis, it afforded two methyl sugars, viz., 2,3,4-tri-*O*-methyl-D-galactose and 2,4-di-*O*-methyl-D-galactose in equimolecular proportions.

The mole proportions of these components were determined by weighing the different pure fractions obtained by column chromatography and by calculating the amounts of the pure components from the mixtures with the aid of specific rotations (vide Experimental Section). The hypoiodite method[6a] could not

TABLE I. ANALYSIS OF THE HYDROLYSATE OF THE METHYLATED GUM (NEUTRAL PART)

	Methyl sugar	R_g*	$[\alpha]_D$	Crystalline derivative	Mole proportion
1	2,3,5-Tri-*O*-methyl-L-arabinose	0.96	−40°	Amide	2.03
2	2,3,4,6-Tetra-*O*-methyl-D-galactose	0.89	+108°	Anilide	3.1
3	2,3,4-Tri-*O*-methyl-D-galactose	0.70	+114°	Anilide	1.0
4	2,4-Di-*O*-methyl-D-galactose	0.46	+86°	Anilide	1.94
5	2-*O*-Methyl-L-arabinose	0.40	+98°	Ph·hydrazone	1.05
6	2-*O*-Methyl-D-galactose	0.28	+79°	Anilide	1.1

* R_g values are with reference to 2,3,4,6-tetra-*O*-methyl-D-glucose in solvent C.

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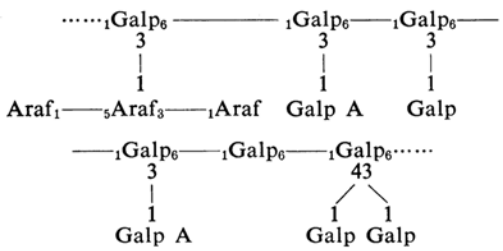
1) S. M. Mukherjee and P. K. Dhar, *J. Sci. & Industr. Res.*, **18B**, 219 (1959).
2) A. K. Bhattacharyya and C. V. N. Rao, *Can. J. Chem.*, **42**, 107 (1964).
3) W. N. Haworth, *J. Chem. Soc.*, **108**, 8 (1915).
4) T. Purdie and J. C. Irvine, ibid., **83**, 1021 (1903).
5) E. L. Falconer and G. A. Adams, *Can. J. Chem.*, **34**, 338 (1956).
6) G. G. S. Dutton and F. Smith, *J. Am. Chem. Soc.*, **78**, 2505, 3744 (1956).
6a) E. L. Hirst, L. Hough and J. K. N. Jones, *J. Chem. Soc.*, **1949**, 928.

be used since it was found difficult to separate the different components quantitatively on paper chromatogram.

From the above results, the following conclusions can be drawn. The characterisation of 2, 3, 5-tri-*O*-methyl-L-arabinose and 2, 3, 4, 6-tetra-*O*-methyl-D-galactose shows that both arabofuranose and galactopyranose residues are present as non-reducing end groups. The presence of 2, 3, 4-tri-*O*-methyl-D-galactose in the trimethyl fraction of the hexose units indicates that the main chain is 1→6 linked. The absence of a dimethyl arabinose indicates that arabinose is not present in the backbone chain of the molecule. The fact that the molecule is highly branched is supported by the characterisation of 2, 4-di- and 2-*O*-methyl-D-galactose and 2-*O*-methyl-L-arabinose. It is also clear that the galactose units which are singly-branched are linked through C_1, C_3 and C_6, while those which are doubly-branched are linked through C_1, C_3, C_4, C_6. The branched arabinose units are, however, linked through C_1, C_3, C_5.

The isolation and characterisation of 2, 4-di-*O*-methyl and 2, 3, 4-tri-*O*-methyl-D-galactose from the aldobiuronic acid fraction of the methylated gum, after reduction and subsequent hydrolysis, indicate clearly that the reducing galactose moiety of the aldobiuronic acid is a part of the main chain and that the uronic acid is present as a single-unit side chain.

From these results and from our knowledge of the structure of the repeating unit of the degraded gum,[2] a possible structure of the repeating unit of the whole gum polysaccharide may be as in Fig. 1.



where Galp = a D-galactopyranosyl unit, Galp A = a D-galactopyranosyluronic acid unit, and Araf = a L-arabofuranosyl unit.

It should be pointed out here that, from the results obtained above, it is not possible to assign the exact sequence of the different groups shown. This repeating unit, however, explains the products obtained from the hydrolysate of the whole gum. It also explains the change in the molar ratio of the compounds of the hydrolysates of the methylated whole gum and of methylated degraded gum shown in Table II.

TABLE II. CHANGE IN THE MOLAR RATIO OF THE METHYL SUGARS IN METHYLATED DEGRADED GUM AND METHYLATED WHOLE GUM

Methyl sugar	Methylated degraded gum	Methylated whole gum
2, 3, 5-Tri-*O*-methyl-L-arabinose	—	2
2, 3, 4, 6-Tetra-*O*-methyl-D-galactose	3	3
2, 3, 4-Tri-*O*-methyl-D-galactose	2	1
2, 4-Di-*O*-methyl-D-galactose	1	2
2-*O*-Methyl-L-arabinose	—	1
2-*O*-Methyl-D-galactose	1	1
Methylated aldobiuronic acid	2	2

During autohydrolysis, the labile arabofuranose units are cleaved out and the degraded gum shows the above behaviour.

The above structure, however, does not explain why the supernatant liquid from autohydrolysis should give only one kind of disaccharide, 3-*O*-L-arabofuranosyl-L-arabinose, and not the other, 5-*O*-L-arabofuranosyl-L-arabinose, which could not be obtained. This may, however, be due to the preferential cleavage of the 1→5 glycosidic bond to the 1→3 bond.

The results of the methylation studies were supported by the data obtained from the periodate oxidation of the gum using periodic acid.[7-9] It was found that the gum consumed 7.58 mol. of the oxidant in 30 hr. (constant), liberating 3.40 mol. of formic acid in 25 hr. (constant) per equivalent of the gum. Considering the facts that (1) a non-reducing galactopyranose unit or galactopyranosyluronic acid unit and a 1→6 linked galactopyranose unit of the backbone chain consume 2 mol. of periodic acid, liberating one mole of formic acid, that (2) galactopyranose units linked through C_1, C_3 and C_6 or C_1, C_3, C_4 and C_6 cannot react with periodic acid, that (3) each non-reducing arabofuranose unit should consume one mole of periodic acid without liberating any formic acid, and, that (4) the arabinose units linked through C_1, C_3, and C_5 do not react at all with periodic acid, the consumption of periodic acid and the liberation of formic acid per equivalent of the gum (assuming the above structure) works out as 7.30 and 3.13 mol. respectively.

The periodate oxidised gum, after reduction with sodium borohydride[10] and the usual

7) F. Smith, *J. Chem. Soc.*, **1951**, 2646.
8) E. L. Hirst, J. K. N. Jones and W. O. Jones, ibid., **1939**, 1880.
9) P. A. Levene and L. C. Kreider, *J. Biol. Chem.*, **120**, 591 (1937).
10) M. Abdel-Akber, J. K. Hamilton, R. Montgomery and F. Smith, *J. Am. Chem. Soc.*, **74**, 4970 (1952).

subsequent treatment, was precipitated with ethanol. The product on hydrolysis gave D-galactose 38.45% and L-arabinose 5.33% (as anhydrosugars). These values are good agreement with the values (36.7% anhydro galactose and 5.98% anhydro arabinose) calculated from the above structure.

The molecular weight of the methylated gum as determined by the light-scattering method was found to be 1.68×10^5. The molecular weight of one repeating unit of the methylated gum, on the basis of the proposed structure, is 2724. Hence, the D.P. of the gum-polysaccharide works out to be 62.

Experimental

Chromatographic separations were carried out using a descending technique with Whatman No. 1 filter papers. The solvent systems employed were: (A) ethyl acetate : pyridine : water (8 : 2 : 1); (B) *n*-butanol : acetic acid : water (4 : 1 : 5) upper layer; (C) *n*-butanol : ethanol : water (40 : 11 : 19); (D) *n*-butanol : ethanol : water (5 : 1 : 4) upper layer; (E) ethyl methyl ketone - water azeotrope; (F) ethyl acetate : acetic acid : water (9 : 2 : 2), and (G) ethyl acetate : acetic acid : water (3 : 1 : 3) upper layer. Aniline oxalate and ammoniacal silver nitrate spray reagents were used in developing the paper chromatograms.

Evaporations were carried out under reduced pressure at bath temperatures of 35~40°C. All the values of specific rotations are at equilibrium.

The isolation and purification of the gum have already been described in details.[2] The purified gum had 8.8% moisture; 0.79% ash; $[\alpha]_D^{30}$ −44° (*c* 0.5, 4% sodium hydroxide solution); equivalent wt., 1150 (acidimetry); 14.5% anhydro uronic acid;[11] 21.7% pentosan;[12] no nitrogen; and 0.51% methoxyl.[13] The gum on hydrolysis gave D-galactose (63.7%) and L-arabinose (19.5%) as estimated by the periodate method.[14]

The Examination of the Supernatant Liquid Obtained during the Autohydrolysis of the gum.—The procedure for the autohydrolysis of gum Jeol has been discussed before.[2] After the precipitation of the degraded gum, the supernatant liquid was collected and concentrated to a small volume. This, on paper chromatographic separation, indicated the presence of arabinose, a trace of galactose and an oligosaccharide (R_{gal} 1.36 in solvent G). The mixture (ca. 500 mg.) was fractionated on a cellulose column (60×3.5 cm.), using solvent A and cutting 20 ml. portions in each tube. The eluate, after paper chromatographic examination, was separated into three fractions.

Fraction I (380 ml.) containing only L-arabinose, was evaporated (410 mg.) and then crystallized from methanol; m. p. and mixed m. p. 152~154°C (with L-arabinose), $[\alpha]_D^{30}$ +108° (*c* 0.8, water). Fraction II (60 ml.) contained a mixture of galactose (trace) and the oligosaccharide (fraction III) (12 mg.) and was not examined further. Fraction III (160 ml.), containing chromatographically-pure oligosaccharide and with $[\alpha]_D^{32}$ +90° (*c* 0.5, water), was evaporated to a sirup (52.6 mg.). The oligosaccharide, on hydrolysis with 1 N sulphuric acid followed by the usual treatment, gave spot of only arabinose on a paper chromatogram. The molecular weight, as determined by the alkaline hypoiodite method, was 274 (calculated for a disaccharide of two pentose units, 282). The sirup (ca. 31.5 mg.) was oxidised with a sodium metaperiodate solution (3 M, 1 ml.) in an acetate buffer (pH 3.7, 49 ml.) in the dark at 0°C. The consumption of periodate became constant in two-and-a-half hours, amounting to 2.08 mol. per mole of the disaccharide.

The Methylation of the Gum.—The purified gum (10 g.) was methylated with dimethylsulphate and sodium hydroxide[3] (four times) and then by Purdie's method[4] (four times), following the method of Falconer and Adams.[5] The fully-methylated gum was a light yellow solid (7.5 g.) with $[\alpha]_D^{32}$ −37° (*c* 0.9, chloroform) and 42.2% methoxyl; it showed no hydroxyl band in the infrared spectrum.

The Methanolysis and Hydrolysis of the Methylated Gum. An Examination of the Neutral Part.—A portion of the methylated gum (2 g.) was refluxed with 2.5% dry methanolic hydrogen chloride (50 ml.) for 16 hr. (constant rotation). The solution was then neutralised (silver carbonate), filtered, and evaporated to a sirup. The sirup was heated with an aqueous barium hydroxide[6] solution (2%, 30 ml.) on a boiling water bath for 4 hr. at 80°C. The solution was neutralised (carbon dioxide gas) and then centrifuged. The resulting solution was deionised with Amberlite IR-120(H), and the acidic component was quantitatively adsorbed on Dowex 1-X4 (acetate) resin. The column was thoroughly washed with water to collect the neutral fraction, which was concentrated to a sirup (5 ml.) and then hydrolysed with 1 N sulphuric acid (50 ml.) at the temperature of a boiling-water bath for 14 hr. (constant rotation). The solution was neutralised (barium carbonate), filtered, deionised, and concentrated to a sirup. The paper chromatographic examination of the sirup using solvents C and D indicated the presence of 2,3,5-tri-*O*-methyl-L-arabinose, 2,3,4,6-tetra-, 2,3,4-tri-, 2,4-di-*O*-methyl-D-galactose 2-*O*-methyl-L-arabinose, and 2-*O*-methyl-D-galactose.

The mixture of methyl sugars (1.0 g.) was resolved on a cellulose column (80×3.5 cm.) using solvent E and collecting 10 ml. in each tube in an automatic fraction-collector. The eluates after chromatographic examination were separated into ten fractions and separately evaporated to sirups. Table III shows the various fractions so obtained.

The Examination of the Fractions and Characterisation of the Methyl Sugars.—*Fraction 1.*—The sirup, $[\alpha]_D^{30}$ −40° (*c* 1, water), was chromatographically pure. The sugar was converted to 2,3,5-tri-*O*-methyl-L-arabonamide through its lactone

11) C. Doree, "The Methods of Cellulose Chemistry," 2nd Ed., Chapman & Hall, London (1947), p. 391.
12) C. Doree, ibid., p. 381.
13) E. P. Clark, "Semi-micro Quantitative Organic Analysis," Academic Press, New York (1943), p. 68.
14) E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, **1949**, 1659.

TABLE III. THE NEUTRAL FRACTIONS OBTAINED AFTER METHANOLYSIS AND HYDROLYSIS OF THE METHYLATED GUM

Fraction	Tube No.	Sugars detectable by paper chromatography	Sugar given on demethyltion[15]	R_g*	$-OCH_3$ %	$[\alpha]_D$	Yield mg.
1	34—40	2,3,5-Tri-*O*-methyl-L-arabinose	Arabinose	0.96	48.24	−40°	138.2
2	41—44	2,3,5-Tri-*O*-methyl-L-arabinose and 2,3,4,6-Tetra-*O*-methyl-D-galactose	Arabinose and Galactose	—	—	+39°	67.0
3	45—54	2,3,4,6-Tetra-*O*-methyl-D-galactose	Galactose	0.89	51.8	+108°	265.1
4	55—58	2,3,4,6-Tetra-*O*-methyl-D-galactose, 2,3,4-Tri-*O*-methyl-D-galactose and probably Di-*O*-methyl-arabinose (trace)	Galactose and Arabinose	—	—	+111°	51.0
5	59—66	2,3,4-Tri-*O*-methyl-D-galactose	Galactose	0.70	41.9	+114°	81.0
6	74—89	2,4-Di-*O*-methyl-D-galactose	Galactose	0.46	29.0	+86°	145.3
7	90—99	2,4-Di-*O*-methyl-D-galactose and 2-*O*-methyl-L-arabinose	Galactose and Arabinose	—	—	+90°	54.2
8	100—109	2-*O*-Methyl-L-arabinose	Arabinose	0.40	18.3	+98°	50.2
9	110—117	2-*O*-Methyl-L-arabinose and 2-*O*-methyl-D-galactose	Galactose and Arabinose	—	—	+86°	13.5
10	118—136	2-*O*-Methyl-D-galactose	Galactose	0.28	15.8	+79°	80.5

* R_g values are with reference to 2,3,4,6-tetra-*O*-methyl-D-glucose in solvent C.

m. p. and mixed m. p. 134～136°C (lit. 136～138°C), $[\alpha]_D^{31}$ +18° (*c* 0.5, water), lit. +20°.[16]

Fraction 2.—The sirup (67 mg.) had $[\alpha]_D^{30}$ +39° (*c* 1, water) and was found by paper chromatography to be a mixture of 2,3,6-tri-*O*-methyl-L-arabinose and 2,3,4,6-tetra-*O*-methyl-D-galactose. On demethylation, the sirup gave galactose and arabinose. From the specific rotation value of the mixture, the amounts of the trimethyl arabinose and tetramethyl galactose were found to be 31.2 mg. and 35.8 mg. respectively.

Fraction 3.—This fraction, with $[\alpha]_D^{30}$ +108° (*c* 1.05, water), was chromatographically pure. The 2,3,4,6-tetra-*O*-methyl-D-galactose was characterised through the crystalline *N*-phenyl-2,3,4,6-tetra-*O*-methyl-D-galactosylamine, m. p. and mixed m. p. 187～189°C,[17] $[\alpha]_D^{30}$ +36° (*c* 0.5, acetone), lit. +39°.[18]

Fraction 4.—The sirup, with $[\alpha]_D^{30}$ +111° (*c* 0.8, water), was found by paper chromatography to be a mixture of 2,3,4,6-tetra- and 2,3,4-tri-*O*-methyl-D-galactose and a trace of methyl arabinose. On demethylation, it gave spots of galactose and arabinose (faint). Disregarding the trace amount of methyl arabinose, the amounts of the tetra- and trimethyl galactose were calculated to be 32.1 and 18.9 mg. respectively from the specific rotation value.

Fraction 5.—The chromatographically-pure fraction had $[\alpha]_D^{30}$ +114°C (*c* 1, water) and was proved to be 2,3,4-tri-*O*-methyl-D-galactose by preparing its aniline derivative, m. p. and mixed m. p. 163～164°C.[19] The melting point depressed on admixture with the aniline derivative of 2,4,6-tri-*O*-methyl-D-galactose.

Fraction 6.—The sirup, with $[\alpha]_D^{30}$ +86° (*c* 1.2, water), was chromatographically pure. On trituration with ether, followed by drying in vacuo, the sirup was converted into a crystalline solid which, on crystallisation from a small volume of ethanol, yielded crystals with an m. p. and mixed m. p. of 98～100°C (with 2,4-di-*O*-methyl-D-galactose monohydrate), lit. 98～99°C.[20] It was further characterised through the crystalline *N*-phenyl-2,4-di-*O*-methyl-D-galactosylamine; m. p. and mixed m. p. 214～215°C, lit. 216°C.[20]

Fraction 7.—The sirup (54.2 mg.), with $[\alpha]_D^{29}$ +90° (*c* 0.6, water), gave galactose and arabinose on demethylation. The mixture, on paper chromatographic examination, indicated the presence of 2,4-di-*O*-methyl-D-galactose and 2-*O*-methyl-L-arabinose. By comparing the specific rotation values of the mixture and of its components, the amounts of dimethyl galactose and monomethyl arabinose were found to be 36.1 and 18.1 mg. respectively.

Fraction 8.—The chromatographically-pure fraction had $[\alpha]_D^{31}$ +98° (*c* 0.9, water) and was identified as 2-*O*-methyl-L-arabinose by conversion to the crystalline phenyl hydrazone; m. p. and mixed m. p. 111～112°C, lit 114°C.[21]

Fraction 9.—The fraction (13.5 mg.) had $[\alpha]_D^{28}$ +86° (*c* 0.5, water) and gave, on demethylation, spots of galactose and arabinose, along with other partially-methylated sugars on a paper chromatogram. The mixture had components which had

15) L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, **1950**, 1702.
16) R. A. Laidlaw and E. G. V. Pereival, ibid., **1949**, 1600.
17) A. K. Mukherjee, D. Chowdhuri and P. Bagchi, *Can. J. Chem.*, **39**, 1408 (1961).
18) P. Andrew, L. Hough and J. K. N. Jones, *J. Am. Chem. Soc.*, **74**, 4029 (1952).
19) M. Abdel-Akher, F. Smith and D. Spriestersbach, *J. Chem. Soc.*, **1952**, 3637.
20) P. Andrews, L. Hough and J. K. N. Jones, ibid., **1954**, 806.
21) J. K. N. Jones, P. W. Kent and M. Stacey, ibid., **1947**, 1341.

the same R_g values as those of 2-*O*-methyl-L-arabinose and 2-*O*-methyl-D-galactose; from the specific rotation value, their amounts were found to be 5.0 and 8.0 mg. respectively.

Fraction 10. — This pure fraction, with $[\alpha]_D^{26}$ +77° (*c* 1.02, water), was proved to be 2-*O*-methyl-D-galactose by converting it to crystalline *N*-phenyl--2-*O*-methyl-D-galactosylamine; m. p. and mixed m. p. 158~159°C, lit. 165°C.[22]

The Examination of the Acid Fraction. — The acid fraction was displaced from the column of Dowex 1-X4 (acetate) resin with 1N sulphuric acid. The neutralisation, deionisation and evaporation of the resulting solution yielded a thick sirup (495 mg.) which had $[\alpha]_D^{32}$ +64° (*c* 1.05, chloroform). A portion of the sirup (ca. 340 mg.) was converted to the methyl ester methyl glycoside by Fischer's method, reduced with lithium aluminium hydride in dry ether,[23,24] and then hydrolysed with 1N sulphuric acid. The hydrolysate, after the usual treatment, was converted to a sirup (264 mg.) which, on paper chromatographic examination using solvents C and D, revealed the presence of 2,3,4-tri-*O*-methyl-D-galactose and 2,4-di-*O*-methyl-D-galactose, with a trace amount of tetramethyl galactose. The mixture (125 mg.) was separated on Whatman No. 3MM filter paper using solvent D. The first fraction (56 mg.) had $[\alpha]_D^{32}$ +107° (*c* 1.1, water) and was identified[2] as 2,3,4-tri-*O*-methyl-D-galactose by preparing the crystalline *N*-phenyl-2,3,4-tri-*O*-D-galactosylamine, m. p. and mixed m. p. 164~166°C, $[\alpha]_D^{31}$ +38° (*c* 0.5, acetone). The second fraction (52 mg.) had $[\alpha]_D^{31}$ +84° (*c* 1.05, water) and was characterised[2] as 2,4-di-*O*-methyl-D-galactose by preparing its aniline derivative, m. p. and mixed m. p. 218~219°C. The amounts of the two components obtained after separation indicate that they are in an equimolecular proportion.

Periodate Oxidation Studies of the Gum.—The gum (110.9 mg.) was dispersed in water (50 ml.) and was treated with a 0.2 M periodic acid solution in water (50 ml.). The oxidation was conducted by shaking the reaction mixture in the dark at 15°C. The liberated formic acid and the periodic acid consumption during the reaction were estimated in the usual way[25] at regular intervals of time. The liberation of formic acid became constant after 25 hr., corresponding to 3.40 mol. (after correction for the titratable acidity of the gum and periodic acid), while the periodate uptake became constant after 30 hr., corresponding to 7.58 mol. per equivalent of the gum.

The periodate-oxidised gum (102.5 mg.) was neutralised (barium hydroxide) and filtered, and to the clear solution sodium borohydride (150 mg.) was added. The reduction was then allowed to proceed for 4 hr. at room temperature. After the usual treatment, the resulting solution was poured into ethanol to precipitate the periodate-oxidised reduced gum, which was triturated with ethanol and then by dry ether and finally dried in vacuo at 40°C. Yield, 62.2 mg. The precipitated polysaccharide (ca. 40 mg.) was hydrolysed with 2N sulphuric acid at the temperature of a boiling-water bath for 24 hr. The amounts of galactose and arabinose left unattacked by periodic acid, as estimated by using D-ribose as a reference sugar, were found (as anhydro sugars) to be 38.45% each.

The Determination of the Molecular Weight of the Methylated Gum.—All measurements of the intensity of scattered light for the molecular weight determination of the methylated gum were carried out with a Brice-Phoenix light-scattering photometer (Model OM 1000 A), using a semi-octagonal cell. The concentrations used were over a range of $(1\sim7)\times10^{-3}$ g./ml., and the working standard method was used to calculate the turbidity, τ. The molecular weight was found to be 1.68×10^5, as calculated by the dissymmetry method[26] assuming the particle-scattering factor of P 90°[27,28] for the random coil.

Summary

The polysaccharide obtained from gum jeol has been shown to be composed of D-galactose, L-arabinose, and D-galacturonic acid. The hydrolysis of the fully-methylated gum yielded 2, 3, 5-tri-*O*-methyl-L-arabinose (2.03 mol.), 2,3, 4, 5-tetra-*O*-methyl-D-galactose (3.1 mol.), 2, 3, 4-tri-*O*-methyl-D-galactose (1 mol.), 2, 4-di-*O*-methyl-D-galactose (1.94 mol.), 2-*O*-methyl-L-arabinoses (1.05 mol.) and 2-*O*-methyl-D-galactose (1.1 mol.) in the neutral fraction of the hydrolysate. The reduced acidic fraction gave 2, 3, 4-tri-*O*-methyl-D-galactose (2 mol.) and 2, 4-di-*O*-methyl-D-galactose (2 mol.). The structural significance has been discussed from the above results and from the results of periodate oxidation studies of the gum. The molecular weight of the methylated gum has also been determined by the light-scattering method.

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