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STRUCTURAL STUDIES OF GUM ARABIC, THE EXUDATE POLYSACCHARIDE FROM *Acacia senegal*[*†]

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ABSTRACT

A 25.182-MHz ^{13}C-n.m.r. spectrum of gum arabic allows unambiguous characterisation of all the C-1 resonances. These assignments have been confirmed by correlation of the modification of the intensities of these signals after controlled acid hydrolysis and characterisation of the released fragments. The resonances of the other carbons have been assigned through partial relaxed T_1 spectra of the polysaccharides obtained by graded degradation of the gum. These results indicate gum arabic to consist mainly of a (1→3)-β-D-galactan core with (1→6)-β-D-galactopyranosyl branches and with α-L-arabinofuranosyl-(1→3)-α-L-arabinofuranosyl and α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyluronic acid groups attached to positions 3 and 6, respectively, of the branch units.

INTRODUCTION

Gum arabic is a highly branched, uronic acid-type heteropolysaccharide produced as an exudate from trees of the genus *Acacia* maintained under unhealthy conditions. In spite of its economic importance and early investigations, a definitive and unambiguous structure is still lacking for this complex natural hydrocolloid. It was established early[3–5] that gum arabic is composed of L-arabinose, D-galactose, L-rhamnose, and D-glucuronic acid in the molar ratios ~3:3:1:1. Subsequent extensive structural studies[6–14] were based on (*a*) the characterisation of oligosaccharides formed at various stages of graded hydrolysis, (*b*) isolation, after Smith degradation, of a linear (1→3)-β-D-galactan, and (*c*) methylation analysis at various stages of degradation.

From these results, it is generally accepted that gum arabic contains a (1→3)-β-D-galactan core with some alternate β-(1→6) linkages. Neutral side-chains of (1→6)-β-D-galactopyranose oligosaccharides and (1→3)-linked L-arabinofuranose or L-arabinopyranose oligosaccharides are located at positions 3 of the core, and

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†For preliminary reports, see refs. 1 and 2.

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acidic side-chains such as α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyluronic acid or 4-*O*-methyl-β-D-glucopyranosyluronic acid groups are attached to positions 6 of D-galactopyranosyl residues. The occurrence of repeating sub-units is still a matter of speculation, although recent results, based on the molecular weights of the oligosaccharides formed during partial degradation[15] and modelling considerations[16], favour a relatively ordered structure. Although the configurations of most of the interglycosidic linkages appear to be well established, mainly from optical rotation data of oligosaccharides obtained by partial hydrolysis, firm assignments based on non-destructive methods are still needed and ^{13}C-n.m.r. spectroscopy has proved to be a valuable tool in this respect. Related relaxation techniques, reflecting relative molecular-mobility parameters, may be of further help for the overall visualisation of this highly branched molecule and we now report on these aspects.

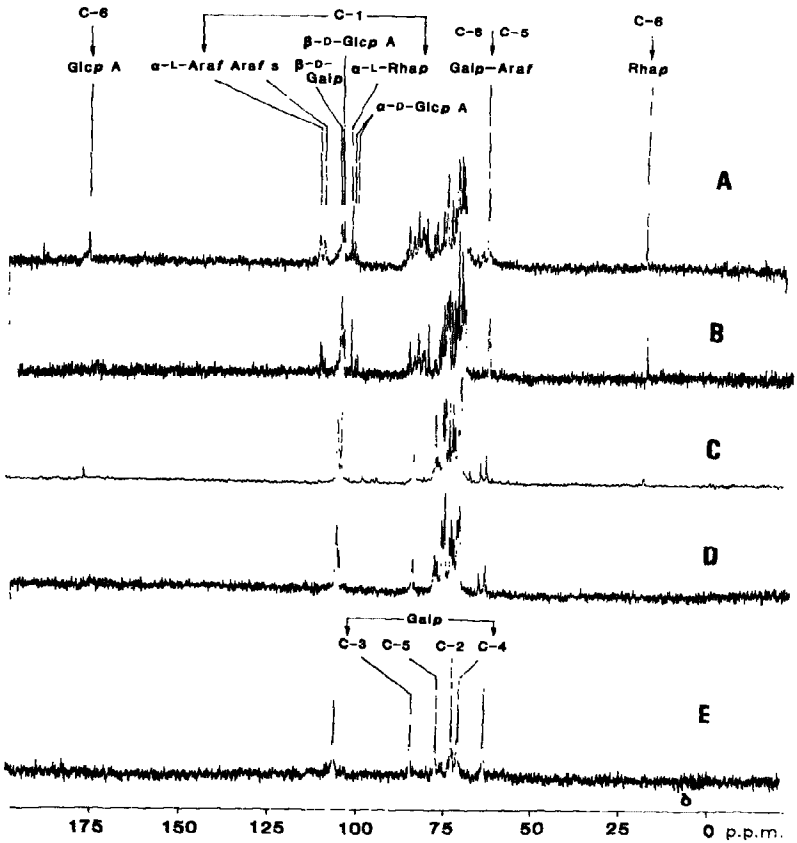


Fig. 1. ^{13}C-N.m.r. spectra: A, gum arabic; B, 23-h autohydrolysed sample; C, 50-h autohydrolysed sample; D, sample autohydrolysed for 50 h and then hydrolysed by 0.1M H_2SO_4 at reflux for 2 h; E, sample resulting from 50-h autohydrolysis followed by carboxyl-reduction[24] and Smith degradation.

TABLE I

^{13}C-N.M.R. DATA

Fig.	*Monosaccharide constituents*	*Chemical shifts (p.p.m.)*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
2B	α-D-Ara*f*-(1→	109.6	82.0	77.5	84.9	62.2	—
	(ref. 19)	(109.3)	(81.9)	(77.5)	(84.9)	(62.4)	
2C	→3)-β-D-Gal*p*-(1→	104.5	71.2	82.7[a]	69.2	75.4	62.0
	(ref. 21)			81.1[b]			
		(104.9)	(71.1)	(82.9)	(69.4)	(75.9)	(61.9)
3B	β-D-Gal*p*-(1→	104.5	71.7	73.7	69.6	76.0	62.0
	(ref. 19)	(104.5)	(71.7)	(73.8)	(69.7)	(76.0)	(62.0)
4B	→4)-β-D-Glc*p*A-(1→	103.7	74.5	77.6	80.1	75.6	175.6
	(ref. 21)	(103.7)	(74.3)	(75.7)	(82.4)	(75.1)	(172.0)
	α-L-Rha*p*-(1→	101.6	71.5		73.3	70.0	17.7
	(ref. 19)	(101.9)	(71.0)	(71.3)	(73.1)	(69.4)	(17.7)

[a](1→3)-β-D-Glc*p*. [b](1→3)-α-L-Ara*f*.

RESULTS AND DISCUSSION

The gum polysaccharide from *Acacia senegal* (syn. *A. verek*), in aqueous solution, gave a well-resolved ^{13}C-n.m.r. spectrum (Fig. 1A), in agreement with previous results[17]. The two signals at extreme fields can be assigned unambiguously to C-6 of L-rhamnopyranose (17.7 p.p.m.) and D-glucuronic acid (175.6 p.p.m.)[17]. In the range for the anomeric carbon resonances (90–110 p.p.m.), at least 7 signals can be resolved and the tentative assignments given in Fig. 1A and Table I are based on literature data[18–21], assuming that L-arabinose, D-galactose, L-rhamnose, and D-glucuronic acid are the only constituents of the gum. Confirmation of most of these assignments was obtained by correlation of the modification of the intensities of these signals after controlled acid hydrolysis and simultaneous characterisation of the resulting fragments by chromatography after dialysis. Thus, when an aqueous solution of the acidic form of the polysaccharide was boiled for 23 h, autohydrolysis released most of the L-arabinose with simultaneous decrease of the signal intensities at 109.3 and 110.4 p.p.m. (Fig. 1B), consequently assigned to C-1 of (1→3)-linked α-L-arabinofuranose residues in terminal and internal positions, respectively. A simultaneous decrease in the intensity of the signal at 110.6 p.p.m., attributed to C-1 of D-glucopyranosyluronic acid residues, also occurred. The known resistance to mild acid hydrolysis of alkyl glycosiduronic acids suggests that some glucuronic acid residues may be linked to acid-labile arabinofuranosyl side-chains. This point is in conflict with results in the literature[22] where glucopyranuronic acid residues were found to be linked exclusively to D-galactose.

Autohydrolysis for 50 h resulted in the modified spectrum shown in Fig. 1C. As expected, signals at 110.4, 109.3 (C-1 of L-arabinofuranose), and 100.6 p.p.m.

(C-1 of L-rhamnopyranose) disappeared, and the latter point was confirmed by the disappearance of the signal at 17.7 p.p.m. for C-6 of 6-deoxyhexoses. Treatment of the resulting polysaccharide with 0.1M sulfuric acid for 2 h enhanced this simplification (Fig. 1D), since only two signals (103.9 and 104.6 p.p.m.) remained in the region for anomeric carbons attributed to D-glucopyranosyluronic acid and D-galactopyranosyl residues. These assignments were confirmed by hydrolysis of this partially degraded polysaccharide with M sulfuric acid, which led to the exclusive recovery of D-galactose and D-glucuronic acid. A further ^{13}C-n.m.r. gated-decoupling spectrum showed, for these anomeric carbons, $^{1}J_{C,H}$ values of 158 and 159 Hz in agreement with the β configuration at each site[23].

Smith degradation of a partially degraded gum, obtained by autohydrolysis for 50 h followed by carboxyl-reduction[24] (Fig. 1E), gave a non-dialysable component which showed six ^{13}C signals (Fig. 1E) that can be assigned to C-1/6 of a (1→3)-linked β-D-galactan, part of the internal core of the gum.

Complete assignment of the non-anomeric ^{13}C resonances in the 60–90 p.p.m. region proved to be difficult, due to overlapping of the signals. Therefore, spectra simplified by partial acid hydrolysis or Smith degradation were used together with spin–lattice relaxation studies. Application of the latter technique in the study of macromolecular dynamics has recently been discussed[25], and relaxation mechanisms in mono- and oligo-saccharides are dominated by the intermolecular dipole–dipole relaxation mechanism[26]. The relaxation rates for oligosaccharides give information about the molecular motion of these molecules and have proved useful for the identification of resonances belonging to the carbons of a particular unit of an oligosaccharide, as well as in the distinction of main-chain components, branch-point positions, or side-chain units in oligo-[25] and poly-saccharides[26]. Both applications of this technique were considered for gum arabic.

A single Smith-degradation on gum arabic yielded a polysaccharide (SD1) having a simplified ^{13}C-n.m.r. spectrum (Fig. 2A) which contained only three C-1 signals, previously assigned to α-L-arabinofuranose, β-D-galactopyranose, and β-D-glucopyranuronic acid residues. The presence of a single C-1 signal for L-arabinose [*cf.* the double signal given by the intact gum (Fig. 1A)] suggested that the (1→3)-linked α-L-arabinofuranosyl side-chains contained no more than 2 units. This point was confirmed after a second Smith-degradation, when the ^{13}C-n.m.r. spectrum (Fig. 3A) of the product (SD2) did not contain a C-1 signal for α-L-arabinofuranose. The remaining C-1 signal of low intensity in Fig. 2A, previously assigned to β-D-glucopyranuronic acid residues, indicated that SD1 contained some D-glucuronic acid residues probably because of incomplete periodate oxidation[22]. Also, SD1 gave no ^{13}C signals for rhamnopyranose, confirming the exclusive external positions of these residues in the native gum.

In order to assign the signals for the non-anomeric carbons in the α-L-arabinofuranose residues in Fig. 2A, a partially relaxed spectrum, using the inversion–recovery pulse sequence [180°–τ–90°–acquisition], was obtained. With a τ value of 0.09 s, the signal of the arabinofuranose C-1, together with four signals of

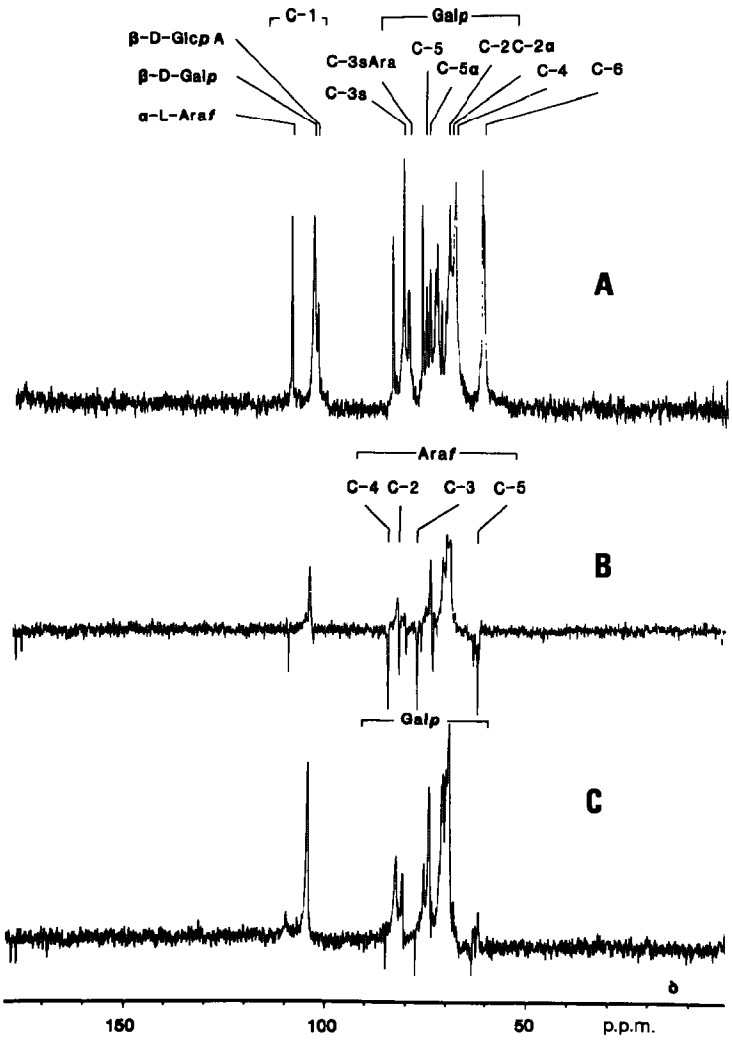


Fig. 2. ^{13}C-N.m.r. spectra of polysaccharide SD1 obtained by one Smith-degradation of gum arabic: A, fully relaxed spectrum; B, partially relaxed spectrum (τ 0.09 s); C, partially relaxed spectrum (τ 0.15 s).

non-anomeric carbons, appeared inverted (Fig. 2B). These resonances for non-anomeric carbons were consequently assigned to C-2/5 of L-arabinose, taking into account the data for methyl α-L-arabinofuranoside[19]. A longer τ value of 0.15 s gave the spectrum in Fig. 2C, which bears some similarity to that (Fig. 1C) of the (1→3)-β-D-galactan core. However, this spectrum was still insufficiently resolved for a complete assignment.

Similar relaxation experiments were performed on SD2 (see Fig. 3A). An initial, short τ value of 0.05 s gave the spectrum in Fig. 3B which contained exclusively six inverted signals with chemical displacements (Table I) comparable to

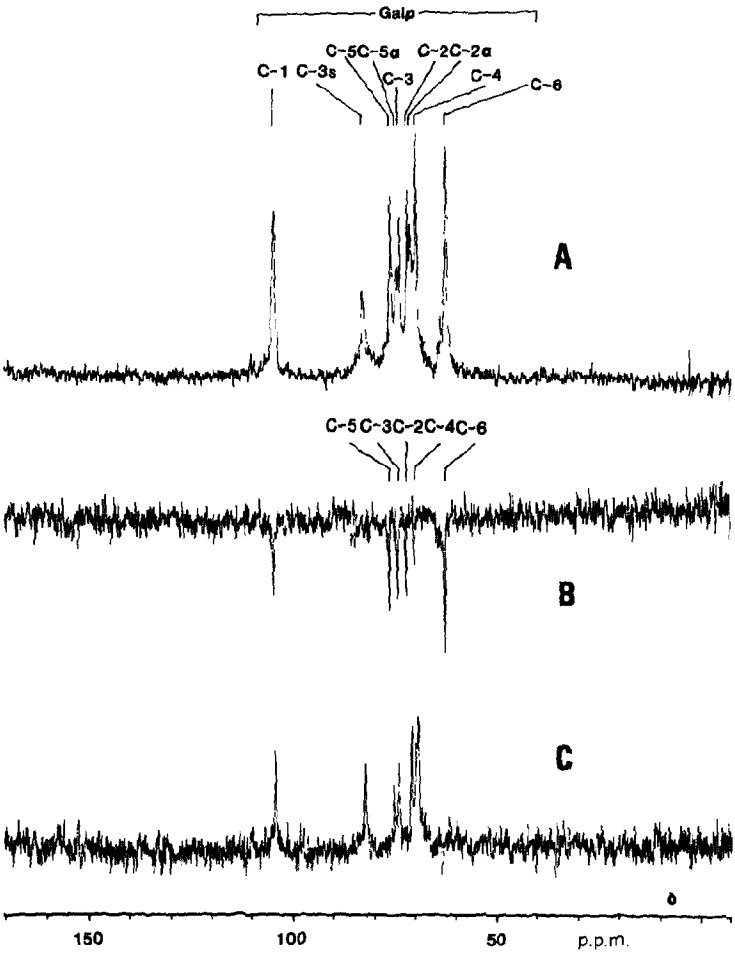


Fig. 3. ^{13}C-N.m.r. spectra of polysaccharide SD2 obtained by two successive Smith-degradations of gum arabic: A, fully relaxed spectrum; B, partially relaxed spectrum (τ 0.05 s); C, partially relaxed spectrum (τ 2.3 s).

those of ^{13}C signals exhibited by methyl α-D-galactopyranoside, and were consequently assigned to an external, more mobile D-galactopyranosyl residue. With a larger τ value (2.3 s), the spectrum in Fig. 3C, due to the galactan core, was obtained. This spectrum is similar to that in Fig. 2C, with an additional resonance at 82.7 p.p.m. Assignments of the D-galactopyranosyl resonances in the spectrum in Fig. 3A were obtained by comparison with the spectrum in Fig. 1E, taking into account the known shifts (7–11 p.p.m.) for *O*-substituted carbons, and a concomitant, smaller upfield shift (1–2 p.p.m.) for the signals of the adjacent carbons. The spectrum in Fig. 3A contains, in addition to the resonances found in the spectra in Figs. 1E [(1→3)-β-D-galactopyranosyl residues)] and 3B, a signal at 74.5 p.p.m.

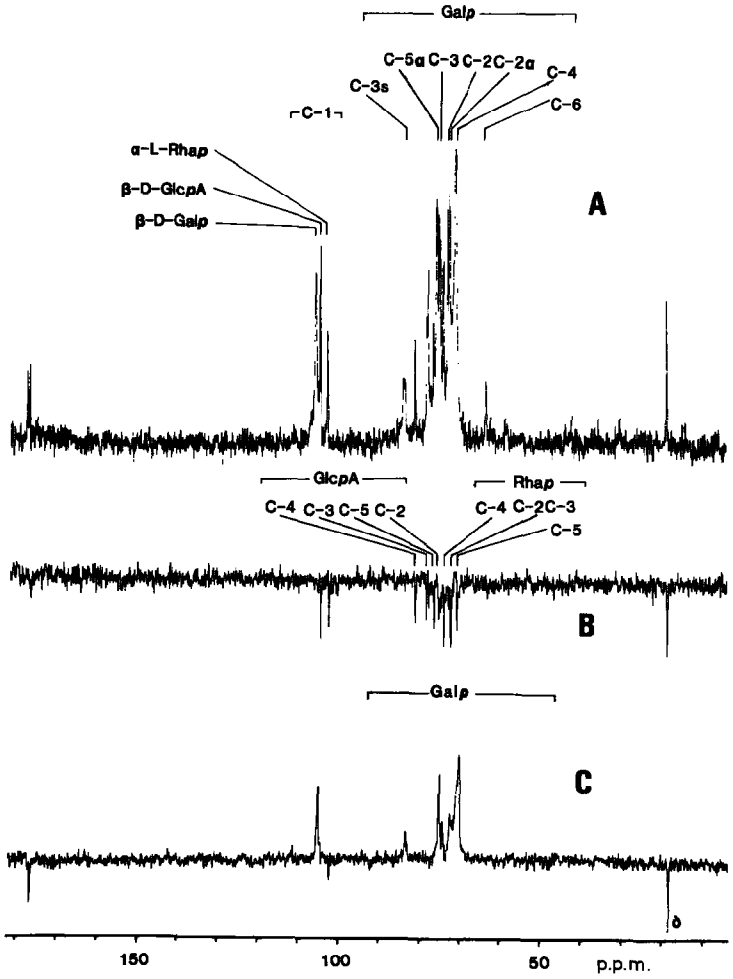
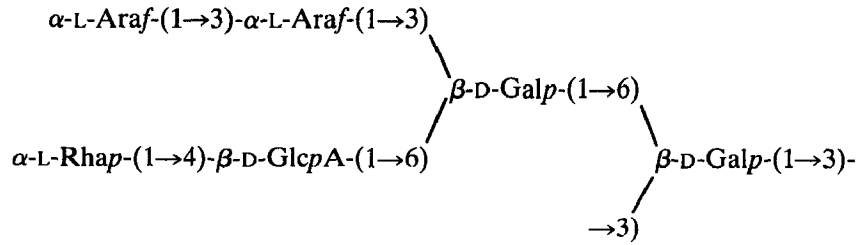


Fig. 4. ^{13}C-N.m.r. spectra of the polysaccharide obtained by hydrolysis of gum arabic with refluxing 4M HCl for 72 h: A, fully relaxed spectrum; B, partially relaxed spectrum (τ 0.05 s); C, partially relaxed spectrum (τ 0.13 s).

which must be due to C-5 of a D-galactopyranosyl residue substituted in a vicinal position. This signal is also found in Fig. 3C and must arise from substitution at C-6. From the spectra in Fig. 3, it becomes clear that two successive Smith-degradations on gum arabic give a branched polysaccharide (SD2) which is composed of a (1→3)-linked β-D-galactan core with single D-galactopyranosyl residues attached to positions 6. Further, it can be inferred from comparisons of the results of the relaxation experiments shown in Figs. 3C and 2C, where there is an extra signal at 82.7 p.p.m. which has been related to 3-substitution of a D-galactopyranosyl residue, that L-arabinofuranosyl units must be linked to O-3 of the 6-*O*-D-galactopyranosyl residues.

Complete removal of the acid-labile arabinofuranosyl residues may be obtained by treatment of gum arabic with 4M hydrochloric acid[13]. As expected, the fully relaxed ^{13}C-n.m.r. spectrum of the resulting polysaccharide (Fig. 4A) exhibits three C-1 resonances for the residual β-D-galactopyranose, β-D-glucopyranuronic acid, and α-L-rhamnopyranose constituents. Of interest is the marked decrease in intensity of the C-6 resonance of D-galactopyranosyl residues at 61.8 p.p.m., which indicates that the D-galactopyranosyl constituents are almost completely substituted at O-6. Furthermore, the loss of the signal at 80.1 p.p.m., seen in the spectrum of Fig. 3C, confirms that this is related to 3-substitution of D-galactopyranosyl residues by L-arabinofuranosyl residues. In the 80–90 p.p.m. region, two resonances seen at 82.5 and 80.1 p.p.m. can be tentatively assigned, respectively, to C-3 of (1→3)-linked β-D-galactopyranosyl residues and C-4 of D-glucopyranosyluronic acid in the side-chain α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyluronic acid constituent. As expected, signals of this entity are displayed in the partially relaxed spectrum of this de-arabinosylated polysaccharide (Fig. 4B), and can be assigned on the basis of literature data[19,27]. The main-chain spectrum, resulting from a 0.13-s relaxation value (Fig. 4C), bears some similarity to the spectra in Figs. 2C and 3C. Thus, it can be concluded that the α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyluronic acid group is in a terminal position and attached to O-6 of D-galactopyranosyl residues.

On the basis of the foregoing results, and data in the literature, it may be concluded that gum arabic possesses an internal (1→3)-β-D-galactan core, with (1→6)-β-D-galactopyranosyl branches and side chains of α-L-arabinofuranosyl-(1→3)-α-L-arabinofuranosyl and α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyluronic acid groups linked, respectively, at positions 3 and 6 of the galactosyl branch-unit (**1**).



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The presence of small proportions of L-arabinopyranose constituents previously reported[13], as well as of other minor components such as 4-*O*-methyl-D-glucuronic acid[22], cannot be ascertained in view of the threshold of sensitivity of ^{13}C-n.m.r. spectroscopy. Good resolution was observed for the ^{13}C-n.m.r. spectrum of gum arabic, suggesting a repetitive sequence, which may be due to the proportion (>50%) of the two external disaccharide sub-units.

The higher relative proportion (38%) of D-galactose reported for gum arabic[22] (38%), as compared to that (33%) implied in **1**, favours the presence of some unsubstituted D-galactosyl groups located at O-6 of the (1→3)-linked β-D-galactan backbone.

From these data, gum arabic most probably does not have strictly regular repeating-units; however, the branched hexasaccharide of **1** may represent the main sub-unit of this highly branched macromolecule.

EXPERIMENTAL

Materials and methods. — A solution of commercial Kordofan gum (Verek sp.), a gift from Iranex S.A. Paris, in water (20 g/100 mL) was filtered through fritted glass, dialysed against water for 24 h, and then freeze-dried. The ^{13}C-n.m.r. spectra of the gum and related polysaccharides were recorded for aqueous solutions at 25.182 MHz, using a Bruker WP-100 spectrometer with D_2O as the internal lock signal. Chemical shifts are given in δ values relative to internal acetone at 31.07 p.p.m. All spectra were recorded at 80°, using a 75° pulse angle and a spectral width of 5681 Hz. Partially relaxed spectra were measured using the sequence [π°–τ–$\pi/2$–T]. Monosaccharides formed during graded hydrolysis of the gum were characterised by using a Waters liquid chromatograph Model 201 U/6000, fitted with a UK6 injector, and a differential refractometer detector R401 connected to a Sefram Servotrace graphic recorder operating at 10-mV full-scale. The pressure was 3.5 MPa and the flow rate was 1 mL/min. Columns (Waters Assoc.) and eluent systems used were (*a*) C18 Radial-pak (8 mm i.d.) and water, and (*b*) μ Bondapak NH_2 (stainless steel, 300 × 3.8 mm i.d.) and acetonitrile–water (80:20). Solvents were distilled and filtered through a Millipore membrane (0.5 μm) Dialysis membrane (Visking, Union Carbide) retained molecular weights higher than 6,000–8,000.

Autohydrolysis of gum arabic. — A solution of the above freeze-dried gum (20 g) in water (1 L) was converted into its free acid form by passing through a column of Amberlite IRN-77 (H^+) resin. The acidic eluate (pH 2.5) was heated under reflux for various times, and the hydrolysates were dialysed against water for 24 h and then freeze-dried to give a white powder (7.7 g, 38% for a 50-h autohydrolysis).

Total acid hydrolysis of gum arabic or partially degraded gum. — A solution of the gum (1 g), or partially degraded gum, in 0.5M sulfuric acid (150 mL) was boiled for 14 h, then neutralised with barium carbonate, filtered, passed through a small column of Amberlite IRN-77 (H^+) resin, and concentrated at 40° under reduced pressure. The components in the syrupy product (900 mg, 90%) were identified by h.p.l.c.

Hydrolysis of autohydrolysed gum arabic. — The product obtained by autohydrolysis of the freeze-dried gum (2 g) was dissolved in 0.1M sulfuric acid (200

mL), and the solution was boiled under reflux for 2 h, then dialysed against water overnight, and freeze-dried to give a white powder (1.8 g, 90%).

Smith degradations. — (*a*) To a solution of the foregoing product (2 g) in water (500 mL) was added 0.1M sodium metaperiodate (500 mL). The mixture was kept at 5° in the dark for 72 h, ethylene glycol (10 mL) was then added, and the solution was dialysed against water overnight. Sodium borohydride (2 g) was then added and, after storage for 1 h at room temperature, the solution was dialysed against water overnight and freeze-dried. A solution of the product in 0.5M trifluoroacetic acid (300 mL) was stored overnight at room temperature, then dialysed, and freeze-dried to give SD1 (1.35 g, 67.5%). A second Smith-degradation gave SD2.

(*b*) A solution of the gum (500 mg), autohydrolysed for 50 h in water (100 mL), was adjusted to pH 4.6 with 0.1M hydrochloric acid, 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide methotoluene-*p*-sulfonate (4 g) was then added in small portions to the solution maintained at pH 4.7. The mixture was stirred for 2 h and sodium borohydride (8 g) was added. After storage for 2 h at room temperature, the solution was dialysed against water for 24 h and then freeze-dried to yield a white powder (440 mg). A portion (200 mg) was dissolved in water (50 mL) and Smith degradation was performed, as described above, using 0.1M sodium metaperiodate (50 mL), sodium borohydride (300 mg), and 0.5M trifluoroacetic acid (100 mL). The product, after freeze-drying, was a white powder (98 mg).

Hydrolysis of gum arabic. — A solution of the gum (2 g) in 4M hydrochloric acid (100 mL) was kept at 20° for 72 h, then dialysed against water, and freeze-dried to give a white powder (1.4 g, 70%).

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