Acacia karroo *Gum.*

By A. J. CHARLSON, J. R. NUNN, and A. M. STEPHEN.

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Acid hydrolysis of *Acacia karroo* gum furnishes L-rhamnose (2%), L-arabinose (36%), D-galactose (50%), and D-glucuronic acid (12%). 3-*O*-β-L-Arabopyranosyl-L-arabopyranose, 4-*O*-α-D-glucuronosyl-D-galactose, and 6-*O*-β-D-glucuronosyl-D-galactose have been isolated from the products of partial hydrolysis. The gum differs markedly in structure from other *Acacia* gums so far examined.

THE compositions of the gums from *Acacia senegal* (Butler and Cretcher, *J. Amer. Chem. Soc.*, **1929**, **51**, 1519), *A. mollissima* (Stephen, *J.*, **1951**, 646), *A. pycnantha* (Hirst and Perlin, *J.*, **1954**, 2622), and *A. cyanophylla* (Charlson, Nunn, and Stephen, *J.*, **1955**, 269) differ in certain respects, though the monosaccharides and the aldobiuronic acid produced on acid hydrolysis are the same for them all. Thus, the equivalent weights and specific rotations of the gums vary from species to species, and the disaccharides isolated after graded hydrolysis differ. The gum of *A. karroo* Hayne. (" doringboom "; Karroo thorn; mimosa), a tree indigenous to South Africa and found extensively in the semi-arid inland regions, has been investigated in order to compare its composition with those of other *Acacia* gums, particularly " gum arabic " types such as *A. senegal* gum.

The equivalent weight (*ca.* 1660) of the gum acid from *A. karroo* is similar to that of the gum acid from *A. mollissima*, but by contrast the specific rotation (+54°) differs in sign from that of any other *Acacia* gum. Autohydrolysis of the gum acid produced a degraded polysaccharide acid of equivalent weight 1270, a mixture of acid oligosaccharides, L-rhamnose, L-arabinose, D-galactose, and two neutral reducing disaccharides. One of these, which was produced in low concentration and was not isolated, moved at the same rate on

paper chromatograms as the galactose-arabinose disaccharide obtained from *A. cyanophylla* and certain varieties of gum arabic (cf. Charlson, Nunn, and Stephen, *loc. cit.*). The other consisted of arabinose units only, and its optical rotation (+208°) and m. p. of the derived phenylosazone (230°) indicated that it was 3-*O*-β-L-arabopyranosyl-L-arabopyranose, obtained previously by Jones (*J.*, 1953, 1672) from larch ε-galactan and by Andrews, Ball, and Jones (*J.*, 1953, 4090) from peach gum and cherry gum. This disaccharide could not be detected amongst the hydrolysis products of *A. cyanophylla* gum, which is understandable in view of the low arabinose content of this gum, and is present apparently in traces amongst the hydrolysis products of *A. mollissima* gum (unpublished work) and "gum arabic, Turc. variety" (Jones, *loc. cit.*).

Hydrolysis of *A. karroo* gum with 0·5N-sulphuric acid gave, in addition to the monosaccharides noted above, a mixture of two aldobiuronic acids in similar amounts. Separation of the acids by partition chromatography on cellulose yielded the expected 6-*O*-β-D-glucuronosyl-D-galactose and a faster-moving acid identified as 4-*O*-α-D-glucuronosyl-D-galactose (α-configuration is indicated by the high specific rotation of both the barium salt of the acid and the fully methylated derivative; cf. A. J. Charlson, Ph.D. Thesis, Cape Town, 1954). The latter substance has been isolated from grape-fruit and lemon gums (Connell, Hainsworth, Hirst, and Jones, *J.*, 1950, 1696). Mixtures of aldobiuronic acids, indicating variety in the mode of linkage of uronic acid to the next monosaccharide unit in a gum, are present in the hydrolysis products of mesquite gum (Cunneen and Smith, *ibid.*, 1948, 1141), lemon gum (Andrews and Jones, *ibid.*, 1954, 1724), and gum myrrh (unpublished work); the mixtures from mesquite gum (Smith, *ibid.*, 1951, 2646) and gum myrrh comprise the 4-*O*-methyl-D-glucuronic acid analogues of the aldobiuronic acids obtained from *A. karroo* gum. White (*J. Amer. Chem. Soc.*, 1954, **76**, 4906) has discussed the structure of sapote gum in the light of his finding that two alkylated aldobiuronates appear among the methanolysis products of the methylated gum.

The tendency of *A. karroo* gum to become insoluble in water when dried and stored has precluded its being examined electrophoretically. The production of two aldobiuronic acids suggests that two different polysaccharides may be present in the gum, and in any event it is purposeless to attempt to express the structure of the gum in terms of a repeating unit containing a single uronic acid unit; the very low rhamnose content (as in *A. pycnantha* gum) further emphasises this. However, expressed as approximate percentages, the quantities of sugars and uronic acid produced on hydrolysis were L-rhamnose (2), L-arabinose (36), D-galactose (50), and D-glucuronic acid (12).

Experimental

Unless otherwise stated, concentration of solutions was carried out at 40°/20 mm., and specific rotations were measured in aqueous solution. Paper chromatograms were run at 27° in butanol–ethanol–water (20 : 1 : 3), ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4) (Jones, *loc. cit.*), or butanol–pyridine–water (9 : 2 : 2).

A. karroo *Gum.*—Crude gum, in the form of nearly colourless, transparent lumps, was collected near Alice in the Eastern Cape Province during autumn, through the courtesy of Mr. H. J. D. Matthews. The gum was converted into the gum acid by the procedure used in the purification of *A. cyanophylla* gum (Charlson, Nunn, and Stephen, *loc. cit.*), yielding a white amorphous powder, $[\alpha]_D$ +54° (*c*, 1·33, as sodium salt) [Found: Sulphated ash, 0·56%; equiv., 1660 (on material dried at 100°/20 mm.)].

Quantitative Hydrolysis.—*A. karroo* gum acid was hydrolysed by 1·5N-sulphuric acid for 15 hr. at 100°, and the products were separated by paper chromatography and analysed by Somogyi's method (*J. Biol. Chem.*, 1952, **195**, 19). Galactose and arabinose were found in the molar ratio 1·2 : 1; rhamnose was present, but in amount too small to estimate with accuracy.

Autohydrolysis.—The gum acid (45 g.) in water (1 l.) was heated on a boiling-water bath for 75 hr., samples being withdrawn and examined qualitatively on a paper chromatogram. Arabinose was detected after 2 hr. and two disaccharides at 3·5 hr.; the slower-moving of these moved at the same rate as the galactose-arabinose disaccharide from *A. cyanophylla* gum, and its intensity did not increase as hydrolysis proceeded. The faster-moving disaccharide increased

in amount with time. Rhamnose appeared after 12 hr. and both galactose and aldobiuronic acid after 17 hr.

A degraded acid (19 g.) was precipitated by pouring the concentrated hydrolysate into ethanol (Found, on material dried at 100°/20 mm.: Equiv., 1270). Hydrolysis of this indicated the presence of galactose and uronic acid units. A mixture of barium salts (4 g.) of low molecular weight and a sugar syrup (24 g.) were recovered from the filtrate.

The sugar syrup was fractionated on cellulose, half-saturated aqueous butanol being used, yielding α-L-rhamnose hydrate (0·9 g.), L-arabinose (15·2 g.), and D-galactose (2·0 g.), which were identified in the usual way, together with a hygroscopic disaccharide (1·6 g.). Elution with water gave a mixture of barium salts (3 g.) of low molecular weight.

Identification of Disaccharide.—This reducing compound had $[\alpha]_D^{18}$ +208° (*c*, 1·7), R_{gal} 0·58 (relative to galactose) in the basic solvent, and R_{gal} 0·72 in the acid solvent, and on hydrolysis of a portion (0·1 g.) in 0·5N-sulphuric acid for 2 hr. at 100°, arabinose only was produced (detected on a paper chromatogram).

The disaccharide formed a phenylosazone, m. p. 230° (decomp.) after recrystallisation from ethanol (Found: C, 56·6; H, 6·4; N, 12·6. Calc. for $C_{22}H_{28}O_7N_4$: C, 57·4; H, 6·1; N, 12·2%). Jones (*loc. cit.*) reports 3-*O*-β-L-arabopyranosyl-L-arabinose as having $[\alpha]_D$ +220° ±10°, R_{gal} 0·69 (basic solvent), 0·79 (acid solvent); osazone, m. p. 235°. The disaccharide crystallised during several months. Methylation of the disaccharide (1·0 g.) afforded a syrup (1·1 g.) having n_D^{20} 1·469, $[\alpha]_D^{20}$ +230° (*c*, 0·79); a portion (0·1 g.) was distilled, the syrup (0·07 g.) having b. p. 130—150°/4 × 10^{-2} mm. (Found: OMe, 50·3. Calc. for $C_{16}H_{30}O_9$: 6OMe, 50·6%).

Hydrolysis of the methylated product (0·5 g.) yielded a syrup (0·48 g.) which exhibited two spots, R_{MG} 0·92 (relative to tetramethylgalactose) and R_{MG} 0·78, and a much fainter spot, R_{MG} 0·60 (basic solvent). Fractionation on cellulose gave: (i) a syrup (0·19 g.), $[\alpha]_D^{19}$ +145° (*c*, 1·1), R_{MG} 0·92, which on bromine oxidation and treatment with phenylhydrazine afforded 2 : 3 : 4-tri-*O*-methyl-L-arabonophenylhydrazide, m. p. 153—155° (lit., m. p. 156°, 158°, 160°); (ii) a mixture of methylated sugars (0·12 g.); and (iii) a di-*O*-methylarabinose (0·11 g.), $[\alpha]_D^{22}$ +120°

Acid (II) was methylated to a crystalline derivative, m. p. 89°, $[\alpha]_D^{22}$ −30° (*c*, 0·9 in $CHCl_3$), identical (mixed m. p.) with the hepta-*O*-methyl methyl ester of 6-*O*-β-D-glucuronosyl-D-galactose obtained from *A. cyanophylla* gum (Charlson, Nunn, and Stephen, *loc. cit.*).

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DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CAPE TOWN.
NATIONAL CHEMICAL RESEARCH LABORATORY,
COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH, PRETORIA.

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