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Note

Some structural studies on degraded *Spondias dulcis* gum

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The gum from the Indian plant *Spondias dulcis* (of the Anacardiaceae family) was dissolved in water, and the polysaccharide was fractionally precipitated with ethanol. The precipitates were washed with acetone, and dried. The major fraction constituted ~90% of the material, had $[\alpha]_D^{26}$ −4°, moved as a single spot in high-voltage electrophoresis, and gave a single peak in ultracentrifugal analysis. Hydrolysis of the polysaccharide with 0.5M sulfuric acid for 16 h at 100°, followed by paper chromatography, gave spots corresponding to galactose, arabinose, and galacturonic acid. G.l.c. analysis of the alditol acetates gave peaks corresponding to galactose and arabinose. The percentages of the different sugars were: galactose, 19.8; arabinose, 48.5; and galacturonic acid, 20%.

The polysaccharide was subjected to autohydrolysis in a boiling-water bath for 60 h, when galactose appeared in the hydrolyzate. The autohydrolysis was therefore stopped before that stage, and the degraded gum was precipitated with ethanol. It was found to be homogeneous by high-voltage electrophoresis and ultracentrifugal analysis, and had $[\alpha]_D^{26}$ −14°. The hydrolyzate of the degraded gum was found to contain galactose, arabinose, and galacturonic acid (by paper chromatography and g.l.c.); the mole ratios of these sugars were found to be 3:3:1. On hydrolysis with 0.05M sulfuric acid, the degraded material gave an aldobiouronic acid which was separated from neutral sugars by use of Dowex-1 X-4 resin. On hydrolysis, the aldobiouronic acid gave galactose and galacturonic acid. The carboxyl-reduced[1], degraded gum gave, on hydrolysis, galactose and arabinose in the ratio of 1.3:1, confirming the presence of galacturonic acid in degraded gum. The latter was methylated by the Hakomori method[2] followed by the Purdie method[3], to yield a fully methylated derivative that, on hydrolysis, gave 2,3,5-tri-*O*-methylarabinose (1.0 mol), 2,3,4-tri-*O*-methylarabinose (0.90 mol), 2,5-di-*O*-methylarabinose (0.91 mol), 2,4,6-tri-*O*-methylgalactose (0.50 mol), 2,4-di-*O*-methylgalactose (0.93 mol), and 4,6-di-*O*-methylgalactose (0.89 mol). The methylated sugars were identified by g.l.c., using authentic samples.

From these results, some structural features of the degraded gum could be

identified. The nonreducing ends of the macromolecule are occupied by arabinofuranosyl and -pyranosyl groups and one of them is possibly linked to O-3 of another arabinofuranosyl residue. The main chain is composed of 1,3-linked galactopyranosyl and galactosyluronic acid residues. The branches containing arabinosyl units are joined to O-6 of one galactopyranosyl residue and to O-2 of another.

During periodate oxidation, 0.48 mol of oxidant was consumed per hexosyl residue. All of the galactose residues, and most of the glycosyluronic acid residues, survived the oxidation, giving additional support for the linkages assigned to different sugar residues.

EXPERIMENTAL

Paper chromatography was conducted on Whatman No. 1 MM paper with the solvent systems (v/v): (*A*) 4:1:5 1-butanol–acetic acid–water (upper layer), and (*B*) 9:2:2 ethyl acetate–acetic acid–water.

A Hewlett–Packard Model 5713A gas chromatograph fitted with a f.i.d. detector and glass columns (1.83 m × 6 mm) packed with (*1*) 3% of ECNSS-M on Gas Chrom Q (100–120 mesh) and (*2*) 3% of OV-225 on Gas Chrom Q (100–120 mesh) were used for g.l.c. Uronic acid was estimated by the carbazole method[4].

The polysaccharide was treated with 1-cyclohexyl-3(2-morpholinoethyl)carbodiimide metho-*p*-toluenesulfonate[1], and the product reduced with sodium borohydride.

For kinetic study, periodate oxidation was carried out in the dark at 4°. The progress of the reaction was monitored spectrophotometrically[5,6].

A Shandon, high-voltage electrophoresis Model L 24 and a Beckman Model L 5-65 Ultracentrifuge (fitted with a Schlieren optical system) were used for testing the homogeneity of the materials.

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