353. *West African Plant Gums. Part I.* Khaya grandifoliola *and* Anogeissus schimperi.

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Gums from *Khaya grandifoliola* (mahogany) and *Anogeissus schimperi* have been subjected to graded hydrolysis and the component sugars examined by paper partition chromatography. Hydrolysis of the former gum yields galactose and a degraded polysaccharide constituted of galactose, rhamnose, and galacturonic acid. The latter gum yields, on hydrolysis, arabinose, galactose, and a degraded polysaccharide containing arabinose, galactose, and glucuronic acid.

Commerical gum gatti is obtained from *Anogeissus latifolia*. On hydrolysis with sulphuric acid it yields L-arabinose and an aldobionic acid (equiv., 352). The gum is reported to contain 50% of pentosan and 12% of galacturonic acid (or galactose) (Hanna and Shaw, *Proc. S. Dakota Acad. Sci.*, 1941, **21**, 78).

The water-soluble gum exuded from the bark of *Anogeissus schimperi* was precipitated from aqueous solution by acidified ethanol as a white powder. The aqueous solution was lævorotatory and did not reduce Fehling's solution. Upward mutarotation on hydrolysis indicated β-linkages. Hydrolysis by N-sulphuric acid liberated arabinose and galactose. The degraded polysaccharide which remained was cleaved by 2N-sulphuric acid to arabinose, galactose, and glucuronic acid. The gum from *Anogeissus schimperi* is thus similar to mesquite gum in composition (Anderson and Sands, *Ind. Eng. Chem.*, 1925, **17**, 1257; *J. Amer. Chem. Soc.*, 1926, **48**, 3172; Anderson and Otis, *ibid.*, 1930, **52**, 4461). The component sugars were detected by descending paper partition chromatography.

Khaya gum was prepared as a white powder from the exudate of *Khaya grandifoliola* by dissolution in weak alkali, acidification, and precipitation with ethanol. The aqueous solution was strongly dextrorotatory, with downward mutarotation on hydrolysis indicating α-linkages in the polysaccharide. Hydrolysis of Khaya gum with N-sulphuric acid liberated galactose, which was converted into mucic acid by nitric acid. The degraded polysaccharide was hydrolysed by 2N-sulphuric acid to galactose, rhamnose, and a uronic acid believed to be galacturonic acid. The identity of the uronic acid is based on the characteristic colour reaction with basic lead acetate and has not been confirmed. The component sugars were detected by paper partition chromatography as described above. In composition, the exudate from *K. grandifoliola* resembles slippery elm (*Ulmus fulva*) mucilage (Gill, Hirst, and Jones, *J.*, 1939, 1469; Tipson, Christman, and Levene, *J. Biol. Chem.*, 1939, **128**, 609).

Experimental

Paper Partition Chromatography.—This was carried out on Whatman No. 1 filter-paper strips in phenol–water medium. The solvent front was permitted to advance 30 cm. from the starting-line at 28°. The positions of the sugars were revealed by spraying with aniline hydrogen phthalate in *n*-butanol and development at 105°. Hexoses and pentoses gave rise to brownish and reddish spots respectively, while rhamnose gave a characteristic lemon-yellow

spot. R_F values varied slightly from one chromatogram to the next but the relative positions of the spots were reasonably constant. In every case where a sugar was indicated by the R_F value the identity was established by running further chromatograms with reference-sugar spots.

Khaya Gum.—The gum softens and swells in cold water and dissolves in hot water with difficulty to give a clear, neutral solution. The crude gum was dissolved in cold sodium hydroxide solution (4%), filtered, acidified with acetic acid, and precipitated by ethanol (1½ vols.). Reprecipitation from acidified solution did not reduce the ash content (10·5%). The gum did not reduce Fehling's solution and gave a negative Millon's test for protein; it had $[\alpha]_D^{28}$ +104° (*c*, 0·50 in 4% NaOH). The naphtharesorcin test for uronic acid was positive.

Graded hydrolysis. (*a*) Khaya gum (2·5 g.; ash, 10·8%) was heated with N-sulphuric acid (250 c.c.) for 7 hours in a boiling-water bath; $[\alpha]_D^{30}$ changed from +100° to +81·5°. The neutralised (barium carbonate), filtered hydrolysate was evaporated under reduced pressure and the residue (2·27 g.) extracted with boiling methanol (4 × 50 c.c.). Evaporation of the extracts gave a semi-crystalline mass (A) (1·0 g.), $[\alpha]_D^{28}$ +76° (*c*, 1·24) in water. This (A) was taken up in water (70 c.c.) and subjected to paper-partition chromatotraphy. The sole spot had R_F 0·45, identical with that of galactose on the same paper. The identity of the sugar was confirmed by oxidation of (A) with nitric acid–water (2 : 1) to mucic acid, m. p. 213—214° (from water).

A portion of the methanol-insoluble barium salt was dissolved in water, acidified with sulphuric acid, filtered, and treated with basic lead acetate. The white precipitate which formed dissolved in an excess of reagent. Heating the precipitate gave a brick-red deposit, indicating presence of D-galacturonic acid.

(*b*) The foregoing barium salt (0·81 g.) was treated with 2N-sulphuric acid (50 c.c.), the whole was filtered, and the filtrate heated for 8·5 hours in a boiling-water bath; $[\alpha]_D^{31}$ changed from +61° to +34°. The hydrolysate, neutralised (barium carbonate), filtered, and evaporated under reduced pressure, was extracted with boiling methanol (4 × 50 c.c.). Evaporation of the extracts yielded crystalline sugars (0·156 g.) which were taken up in water (50 c.c.) and analysed on the paper-partition chromatogram as before. Two spots were developed with R_F 0·45 and 0·64 respectively, identical with galactose and rhamnose on the same paper.

Anogeissus *Gum.*—The gum was precipitated from aqueous solution by ethanol (1½ vols.), acidified by acetic acid, as a white flocculum which dried to a white powder (ash, 3·2%). Reprecipitation from acid reduced the ash content to 2·4%. The aqueous solution gave a positive naphtharesorcin test for uronic acid and was strongly lævorotatory $[\alpha]_D^{31}$ *ca.* −64° ($c = 0·23$). The gum did not reduce Fehling's solution and gave a negative Millon's test for protein.

Graded hydrolysis. (*a*) *Anogeissus* gum (5 g.; ash, 2·4%) was heated with N-sulphuric acid (250 c.c.) for 11 hours on a boiling-water bath; $[\alpha]_D^{30}$ became +25° (const.). During hydrolysis a brown flocculent substance (1·4%) separated and was filtered off. This was presumed to be lignin. The hydrolysate was neutralised (barium carbonate) and filtered, and the filtrate evaporated to dryness (5·02 g.) under reduced pressure and extracted with boiling methanol (4 × 150 c.c.). Evaporation of the methanol extracts gave a syrup (2·68 g., 53·6%). Analysis of the insoluble barium salt gave: Ba, 20·3%; OMe, 0; equiv., *ca.* 343.

The syrup (2·68 g.) in water (100 c.c.), analysed by paper-partition chromatography, gave two spots having R_F 0·45 and 0·56 respectively, identical with galactose and arabinose respectively on the same paper.

The basic lead acetate test, applied as for Khaya gum, gave a cream-coloured precipitate which became yellow-brown on heating, indicative of glucuronic acid.

(*b*) The barium salt (2·0 g.) was treated with 2N-sulphuric acid (200 c.c.), the whole filtered, and the filtrate heated for 7 hours in a boiling water bath; $[\alpha]_D^{30}$ (−17·5°) changed to −7·0°. The hydrolysate was neutralised (barium carbonate) and filtered, and the filtrate evaporated to dryness under reduced pressure and extracted with boiling methanol (4 × 50 c.c.). Evaporation of the extracts gave a residue (0·2 g.) which was chromatographed in water (10 c.c.) as before. Two spots were developed, with R_F 0·46 and 0·57 respectively, identical with galactose and arabinose on the same chromatogram.

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