201. *The Constitution of Egg-plum Gum. Part I.*

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The gum exuded on the bark of the egg-plum has been examined and shown to consist of *l*-arabinose (3 parts), *d*-xylose (1 part), *d*-galactose (3 parts), and *d*-glucuronic acid (1 part). The aldobionic acid which is present in the portion of the gum molecule more resistant to acidic hydrolysis is *d*-glucuronosido-6-*d*-galactose identical with the aldobionic acid component present in gum arabic. The oxidation of the gum with potassium periodate has been studied.

In common with many other fruit trees of the family *Rosaceæ* the egg or yellow Pershore plum tree forms a gum during the months of August and September. The gums from several other trees have already been examined (see Hirst and Jones, *J.*, 1946, 506) and it was of interest to determine whether Pershore plum gum has a similar constitution. The gums obtained from exudation usually contain small amounts only of nitrogenous materials, which may be part of the enzyme system originally responsible for their synthesis (M. Stacey, private communication). They are salts of acidic polysaccharides, the acidity being due to the presence of *d*-glucuronic or *d*-galacturonic acids or of their methyl ethers. *d*-Galactose and *l*-arabinose appear to be invariable constituents, whilst *d*-mannose, *d*-xylose, and *l*-rhamnose have also been detected in some plant gums.

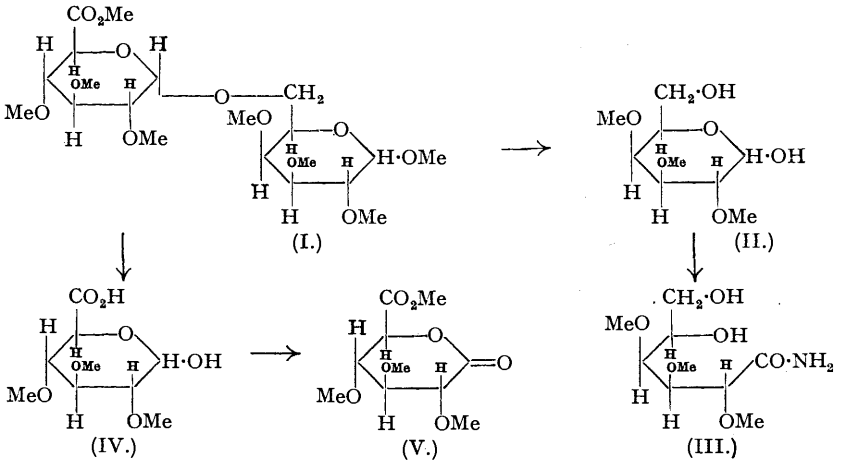
Purified ash-free Pershore plum gum is a white powder soluble in water giving an acidic solution which does not reduce Fehling's solution. So far as present evidence is available the gum so prepared appears to be a homogeneous substance, and attempts to extract from it by solvents fractions differing in elementary and physical properties have been unsuccessful. Gums obtained from several trees in the same area (Worcestershire) all have the same physical properties. The possibility remains, however, that the type of gum exuded by the tree may be dependent upon the type of stock on which the tree is grafted rather than upon the type of plum produced. Further work will be necessary before this can be settled.

The analytical figures for uronic acid residues (14·7%) and furfuraldehyde (25·5%) were obtained by boiling the polysaccharide with 12% hydrochloric acid and determining the amounts of carbon dioxide and furfuraldehyde formed. From these results estimates can be made of the pentose and the uronic acid content of the gum. An aqueous acidic solution of the ash-free polysaccharide undergoes graded hydrolysis on heating at 100°, the sugars obtained after hydrolysis consisting of a mixture of *l*-arabinose and *d*-xylose in the approximate proportion of 3 to 1. The remainder of the polysaccharide consists of *d*-galactose and *d*-glucuronic acid, since on

hydrolysis with N-sulphuric acid crystalline *d*-galactose is obtained together with an aldobionic acid having the structure *d*-glucuronosido-*d*-galactose (1 : 6 linkage) identical with the aldobionic acid in gum arabic. This structure, therefore, is an important feature in the mode of construction of the sugar residues in the repeating unit of the gum. It follows that Pershore plum gum resembles gum arabic, rather than damson or cherry gum (cf. Smith, *J.*, 1940, 1035), and in common with many other gums so far examined it contains a repeating unit consisting of two molecules of galactose united to an aldobionic acid. It is to be remembered, however, that owing to the difficulty encountered in isolating the aldobionic acid component of the gum in quantitative yield the possibility remains that some aldobionic acid other than 1 : 6-*d*-glucuronosido-*d*-galactose may be a component of the gum molecule. Conclusive proof is furnished below, however, of the presence of 1 : 6-*d*-glucuronosido-*d*-galactose as a part of the gum molecule.

The proof of the structure of the aldobionic acid follows from the observation that on methylation followed by hydrolysis of the methylated product (I), two products are obtained, namely, 2 : 3 : 4-trimethyl *d*-galactose (II), identified as its crystalline anilide and as the crystalline amide of 2 : 3 : 4-trimethyl *d*-galactonic acid (III), and 2 : 3 : 4-trimethyl *d*-glucuronic acid (IV), identified as the methyl ester of 2 : 3 : 4-trimethyl *d*-saccharolactone (V).

A quantitative estimation of the various sugars produced on hydrolysis of the original Pershore plum gum indicates that they were combined in the following proportions : *d*-glucuronic acid (1 part) ; *d*-galactose (3 parts) ; *l*-arabinose (3 parts) ; *d*-xylose (1 part).



When the gum is oxidised with potassium periodate under mild conditions, designed to prevent over-oxidation (see Brown, Dunstan, Halsall, Hirst, and Jones, *Nature*, 1945, **156**, 785) approximately one mol. of formic acid is produced and five mols. of periodate are consumed per equivalent of approximately 1220. The resulting oxidised polysaccharide, on being boiled under standard conditions with 12% hydrochloric acid, gives furfuraldehyde (10·8%) in a much diminished yield. This proves that some of those sugar residues in the original unoxidised polysaccharide which yield furfuraldehyde on distillation with hydrochloric acid have been destroyed during the oxidation. Since under the conditions of oxidation there is no continual rise in formic acid titre followed by a subsequent liberation of iodine, the glucuronic acid residue is not an end group (see Brown, Dunstan, Halsall, Hirst, and Jones, *loc. cit.*).

The oxidised polysaccharide on hydrolysis gives some *l*-arabinose (estimated as its benzoylhydrazone), but xylose could not be detected (see Breddy and Jones, *J.*, 1945, 738). The yields of *d*-galactose and *l*-arabinose indicated that at least 1·5 mols. of *d*-galactose and 0·5 mol. of *l*-arabinose per equivalent of 1220 are not oxidised by the periodate and therefore cannot possess adjacent hydroxyl groups in their combination in the gum molecule.

An examination of the product isolated from the reaction between the gum and triphenylmethyl chloride in pyridine shows that there are approximately four primary alcohol groups (Method of Linstedt, *Arkiv Kemi, Min. Geol.*, 1945, **20** *A*, No. 13) per equivalent of 1220.

Experimental.

Purification of Egg-plum Gum.—The gum, which resembled damson and cherry gums in properties, was purified by precipitation with alcohol from aqueous solutions to which hydrochloric acid had been

added (for further details see Hirst and Jones, *J.*, 1938, 1177). The gum gave no precipitate with calcium or copper salts but gave a white precipitate on addition of a large excess of thallium hydroxide. It was unaffected by takadiastase and pectinase at pH 7 at 35°. Two samples were prepared: (*A*) from gum collected from several different trees in two orchards, (*B*) from gum collected off one tree (see Table).

	Gum *A*.	Gum *B*.
$[\alpha]_D^{20°}$ (*c*, 2·4 as the sodium salt in water)	−27°	−25°
Equiv. (by titration with 0·1N-sodium hydroxide)	1228	1215
Furfuraldehyde	26%	25%
Uronic anhydride	—	14·7%
Galactan (from mucic acid determinations)	43%	44%

The samples from different trees are therefore substantially the same. The purified gum had a small iodine number (1·0 g. required 2·5 c.c. of 0·1N-iodine). [Found (crude gum): OMe, trace; N, nil.] The purified gum had a small methoxyl content (2·0%), probably owing to esterification during the purification process. Furfuraldehyde and uronic anhydride were determined after treatment of the purified polysaccharide with boiling 12% hydrochloric acid (Found: furfuraldehyde, 25·5; uronic anhydride or 2-ketohexonic acid, 14·7%). Methylpentose appears to be absent. [A substance yielding 14·7% of uronic anhydride or 2-ketohexonic acid and containing no other acidic residues should have an equivalent of 1197. Found by titration of the gum with alkali: equiv., 1222 (mean of two values).] This proportion of uronic anhydride accounts for 3·7% of the total furfuraldehyde, leaving 21·8% of furfuraldehyde contributed by the pentosan part of the polysaccharide, and since the greater part of the pentose present is *l*-arabinose (see below), the calculated anhydroarabinose content of the gum is approximately 44% (Calc. for a polysaccharide containing four pentosan units per repeating unit of equivalent 1190, 44·3%). Anhydrogalactose (estimated after oxidation to mucic acid), 43%.

Graded Hydrolysis of Egg-plum Gum.—(a) Egg-plum gum (50 g.) was heated with water (1½ l.) at 90—95°, the acidity of the solution being sufficient to bring about slow graded hydrolysis; the reaction was followed by polarimetric and iodometric observations: $[\alpha]_D^{20°}$ −27° (initial value); −24° (40 mins.); −9° (3·1 hrs.); +32° (15·5 hrs.); +41° (22 hrs.); +47° (34 hrs.); +50° (50 hrs.). A much slower hydrolysis continued beyond this stage. The increase in iodine titre was followed by titration of portions of the solution with 0·1N-iodine by Baker and Hulton's method (*Biochem. J.*, 1920, **14**, 754). Initial value (in c.c. 0·1N-iodine, calculated for 1 g. of gum) 2·5 c.c.; 6 c.c. (40 mins.); 15·5 c.c. (3·1 hrs.); 54 c.c. (15·5 hrs.); 58 c.c. (22 hrs.); 66 c.c. (34 hrs.); 72·6 c.c. (50 hrs.). The solution was evaporated at 40°/12 mm. to 500 c.c. and poured into alcohol (1½ l.); it then gave an alcohol-insoluble polysaccharide (*A*) (22·5 g.) which was washed with alcohol.

(b) *Reducing sugars obtained by graded hydrolysis.* The filtrate from (*A*) on concentration at 40°/12 mm. gave an acidic syrup which was dissolved in water, neutralised with barium carbonate, and filtered, and the filtrate poured into alcohol with stirring. The precipitated barium salt (*B*), which appeared to be the barium salt of the polysaccharide (*A*) which had escaped precipitation, was filtered off and the filtrate evaporated at 40°/12 mm. to a syrup which crystallised on standing. The crystalline solid (10·4 g.) was triturated with methyl alcohol and filtered off; it was identified as slightly impure *l*-arabinose, m. p. 154°; $[\alpha]_D^{20°}$ +96° (*c*, 3·8 in water; equilibrium value); diphenylhydrazone, m. p. 194°. The filtrate from the crystalline solid on evaporation gave a syrup (*C*) (15·2 g.) which had $[\alpha]_D^{20°}$ +38° and contained some oligosaccharide, since the iodine titre indicated the presence of only 9·3 g. of pentose. A furfuraldehyde determination indicated the presence of some 10·0 g. of pentose, whilst an arabinose estimation by means of diphenylhydrazine indicated the presence of approximately 5·0 g. of *l*-arabinose. Mucic acid was isolated after oxidation of a portion of the syrup with nitric acid, proving the presence of some 2·4 g. of galactose (free or combined). The syrup underwent further hydrolysis on heating with 0·5N-sulphuric acid for 1 hour. The optical rotation became constant at +60° and the iodine titre on a portion of the solution (*A*) showed that approximately 15 g. of reducing sugars were now present in solution. An estimation by means of diphenylhydrazine now showed the presence of 5·8 g. of *l*-arabinose, an increase of only 0·8 g. It can be inferred, therefore, that the oligosaccharide originally present contained *d*-galactose and *d*-xylose since the increase in reducing power of the solution is not due to increase of *l*-arabinose content but to an increase of *d*-galactose and *d*-xylose. A portion of the solution (*A*) after hydrolysis was neutralised with barium carbonate and filtered, and the filtrate evaporated to a syrup. *l*-Arabinose was removed from this syrup as its diphenylhydrazone, and the non-crystalline diphenylhydrazones remaining were then decomposed by warming with form aldehyde solution in the presence of acetic acid. The mixture was exhaustively extracted with ether and the aqueous solution evaporated to a syrup. [A portion of this gave the characteristic crystalline derivative of xylose, m. p. 210°, with a methyl alcoholic solution of benzaldehyde (see Breddy and Jones, *J.*, 1945, 738).] The syrup was boiled for 4 hours with 4% methyl alcoholic hydrogen chloride, and the solution was then neutralised with silver carbonate, filtered, and evaporated to a syrup which was methylated first by the thallium method (Menzies, *J.*, 1926, 937), and then with Purdie's reagents. The methylated sugars (4·0 g.) were distilled in a vacuum and gave a fraction (3·6 g.), b. p. 100° (bath temp.)/0·1 mm.; $n_D^{18°}$ 1·4438; $[\alpha]_D^{20°}$ +53° in water. This fraction was hydrolysed with N-hydrochloric acid (50 c.c.) on the boiling water-bath. $[\alpha]_D^{20°}$ fell from +53° to +44°. The free sugars were worked up in the usual manner and distilled in a vacuum; the distillate then crystallised. 2 : 3 : 4-Trimethyl *d*-xylose was recognised by its m. p. and mixed m. p. 91°, after recrystallisation from ether. The non-crystalline sugars gave some tetramethyl galactose anilide on heating with alcoholic aniline. This result, taken in conjunction with reducing values, furfuraldehyde yields, rotational values, and yield of *l*-arabinose diphenylhydrazone, indicates that the sugars produced on autohydrolysis consist of *l*-arabinose and *d*-xylose in the approximate proportion of three to one and that a small amount of galactose is also produced during the hydrolysis. A polysaccharide of equivalent weight 1222 and containing this amount of arabinose would yield 36·8% of arabinose on hydrolysis (Found: arabinose content, 32·4%).

(c) *Examination of the barium salt* (B). The barium salt (*B*) (10·4 g.) was obtained as a white powder

easily soluble in water, giving a yellow neutral solution, $[\alpha]_D^{20°}$ +4° (*c*, 3·3 in water). OMe, 3·0% (probably derived from adsorbed alcohol). It contained 11% of barium, gave 8·3% of furfuraldehyde on boiling with 12% hydrochloric acid, and on oxidation gave mucic acid equivalent to the presence of 50% of galactan. It was slightly reducing to Fehling's solution and reduced alkaline iodine (1 g. required 40·5 c.c. of 0·1N-iodine). On being heated with N-sulphuric acid for 3½ hours the barium salt underwent hydrolysis with an increase in iodine titre; initial value (in c.c. of 0·1N-iodine per 1 g. of barium salt) 41 c.c.; 58 c.c. (1½ hrs.); 65·4 c.c. (2 hrs.); 70·7 c.c. (3 hrs.); 74·4 c.c. (3½ hrs., constant value). The change in rotation was not observable owing to the colour of the solution. The solution was neutralised with barium carbonate, filtered, and evaporated to a syrup, which was extracted with methyl alcohol. Concentration of the extracts gave a syrup which soon crystallised. Trituration with alcohol gave crystalline *d*-galactose, $[\alpha]_D^{20°}$ +78° in water, m. p. and mixed m. p. 164°, in 42% yield calculated on the weight of the syrup isolated. (6·65 G. of barium salt gave 2·7 g. of syrup.) The non-crystalline barium-free residue showed $[\alpha]_D^{20°}$ +45° (*c*, 1·22 in water) and was 50% galactose (calc. on the yield of mucic acid obtained after oxidation with nitric acid under standard conditions). Mannose appeared to be absent since no mannose phenylhydrazone could be isolated after treatment of a portion of the non-crystalline syrup with phenylhydrazine solution. The remaining sugar was not identified but may have been *d*-xylose. The above figures show that hydrolysis of the barium salt with N-acid produced 29% of *d*-galactose calculated on the weight of the original barium salt.

The barium salt (3·40 g.) remaining after methyl alcoholic extraction was obtained as a white powder, very soluble in water, giving a yellow solution which reduced Fehling's solution vigorously on boiling. 1 G. of barium salt reduced 39 c.c. of 0·1N-iodine; this is equivalent to a molecular weight of 512. The solution showed $[\alpha]_D^{20°}$ +4° (*c*, 1·0 in water) (Found: OMe, 3·0%, but this value is probably not significant). The barium content of the salt was 15·7%, and on oxidation with nitric acid, mucic acid was produced, in amount showing the presence of some 40% of galactose residues (Calc. for the barium salt of an aldobionic acid; Ba, 16·2; galactose residues, 42%).

(d) *Polysaccharide* (A). This material (22·5 g.) was obtained as a white powder, easily soluble in water giving a brown solution with an acidic reaction to Congo-red. On boiling it with 12% hydrochloric acid, furfuraldehyde (8·1%) and carbon dioxide (equivalent to the presence of 26·0% of uronic anhydride) were evolved. $[\alpha]_D^{20°}$ +24° (in water, *c*, 0·7). The polysaccharide on being heated with nitric acid (*d* 1·2) gave mucic acid equivalent to the presence of some 50% of anhydrogalactose; this figure is low owing to the difficulty experienced in hydrolysing polysaccharide (*A*) completely. The equivalent (by titration with 0·1N-sodium hydroxide) was 640 (Calc. for a repeating unit containing three hexose residues and a uronic acid residue, 662). On titration with alkaline iodine by the method of Bergmann and Machemer, 1 g. of polysaccharide (*A*) required 23 c.c. of 0·1N-iodine.

Polysaccharide (*A*) (1·49 g.) underwent hydrolysis on heating at 90° with N-sulphuric acid (50 c.c.). $[\alpha]_D^{20°}$ changed from +28° (initial value) to +30° (3 hrs., constant value). The iodine titre (in c.c. of 0·1N-iodine per g. of polysaccharide) was 23 c.c. (initial value); 47 (½ hr.); 57 (1 hr.); 73 (2 hrs.); 75 (3 hrs.). The cooled solution was neutralised with barium carbonate, filtered, and evaporated to dryness, and the residue exhaustively extracted with alcohol. Concentration of the extracts gave crystalline *d*-galactose (0·4 g.), m. p. 164°, $[\alpha]_D^{20°}$ +80° (*c*, 1·3 in water). The residual barium salt showed $[\alpha]_D^{20°}$ ±0° (*c*, 2·0 in water). On oxidation with nitric acid (*d* 1·2) it gave mucic acid equivalent to the presence of some 50% of anhydrogalactose, and contained 16·3% of barium (Calc. for a barium aldobionate: Ba, 16·2%).

The barium salt of the aldobionic acid from polysaccharide (*A*) underwent further hydrolysis with much decomposition on being heated at 95° with 4N-sulphuric acid for 24 hours. From the solution, after neutralisation with barium carbonate and filtration, *d*-galactose was obtained in crystals, m. p. 163°, $[\alpha]_D^{20°}$ +77° (*c*, 1·1, in water), and as its phenylmethylhydrazone, m. p. 190°. The barium salt of the uronic acid was identified as barium glucuronate (see below). The total percentage yields of *d*-galactose and barium glucuronate isolated were small, but the proof of the presence of these two compounds combined as an aldobionic acid is furnished by a study of the hydrolysis products of the methylated aldobionic acid.

Methyl heptamethyl aldobionate. The barium salt of the aldobionic acid (3·3 g.) was dissolved in water and the barium precipitated as sulphate by the addition of the calculated quantity of 0·1N-sulphuric acid. The solution was filtered, and the filtrate evaporated to a syrup which was simultaneously esterified and converted into the glycoside by boiling with 2% methyl alcoholic hydrogen chloride for 20 hours. This time of esterification was too long, since much hydrolysis to monosaccharides had taken place. The solution was neutralised with silver carbonate, filtered, and evaporated to a syrup which was methylated by means of thallium hydroxide and methyl iodide in the usual manner (for details, see Hirst and Jones, *loc. cit.*). The methylated material was extracted with acetone, the solvent boiled off, and the residual syrup (2·85 g., $n_D^{17°}$ 1·4545) distilled in a vacuum giving:

Fraction I (2·0 g.). Mainly monosaccharides, b. p. 130° (bath temp.)/0·001 mm.; $n_D^{20°}$ 1·4495.

Fraction II (0·69 g.). Methyl heptamethyl aldobionate, b. p. 180° (bath temp.)/0·001 mm.; $n_D^{20°}$ 1·4680; $[\alpha]_D^{20°}$ +40° (*c*, 1·3 in water) (Found: OMe, 51·3; equiv., 470. Calc. for $C_{20}H_{36}O_{12}$: OMe, 53·0%; equiv. 468).

The methyl heptamethyl aldobionate (Fraction II) (0·67 g.) was hydrolysed by boiling it with 2N-hydrochloric acid (50 c.c.) for 10 hours. The rotation ($[\alpha]_D^{20°}$) rose from +40° to +46° in 3 hours, after which the solution became too dark for polarimetric observation. The cooled solution was neutralised with silver carbonate and filtered before and after the passage of hydrogen sulphide. The solution was then neutralised with barium carbonate and filtered, and the filtrate evaporated to a syrup which was exhaustively extracted with ether. The extracts on concentration gave a syrup {0·27 g.; $[\alpha]_D^{20°}$ +65° (*c*, 1·97 in water); OMe, 41%} which was mainly 2 : 3 : 4-trimethyl *d*-galactose, since after heating a portion of it with alcoholic aniline, the characteristic 2 : 3 : 4-trimethyl *d*-galactose anilide, m. p. and mixed m. p. 169°, was isolated. The rotation of the isolated sugar is low, probably because of contamination with a little 2 : 3 : 5-trimethyl *d*-galactose due to methyl furanoside formation on boiling the aldobionic acid with methyl alcoholic hydrogen chloride (cf. Challinor, Haworth, and Hirst, *loc. cit.*). The

sugar on oxidation with bromine water gave a lactone, $[\alpha]_D^{20°}$ +95° in water (initial value), which with liquid ammonia gave 2 : 3 : 4-trimethyl *d*-galactonamide, m. p. and mixed m. p. 165°.

The barium salt remaining after ether extraction was dissolved in water and barium removed as sulphate. The trimethyl *d*-glucuronic acid remaining in solution was oxidised with bromine water and the 2 : 3 : 4-trimethyl *d*-saccharic acid isolated in the usual manner and esterified with methyl alcoholic hydrogen chloride, and the dimethyl ester distilled in a vacuum; b. p. 120° (bath temp.)/0·01 mm. The distillate crystallised on standing. After separation on a tile, the methyl ester of 2 : 3 : 4-trimethyl *d*-saccharolactone was obtained, m. p. 110° not depressed on admixture with an authentic sample. This aldobionic acid was therefore *d*-glucuronosido-1 : 6-*d*-galactose.

Oxidation of the Gum with Potassium Periodate.—(*a*) The neutral gum (0·25 g.) was dissolved in water (250 c.c.) containing potassium chloride (1 g.) and sodium periodate (20 c.c.; 0·3M) and shaken for 10 days at 15°. Portions (10 c.c.) were taken out at intervals, ethylene glycol was added to destroy excess of periodate, and the formic acid was titrated with 0·01N-barium hydroxide [Titre: 0·65 c.c. (24 hrs.); 0·85 c.c. (72 hrs.); 0·9 c.c. (96 hrs.); 0·9 c.c. (192 hrs. constant)].

(*b*) The gum (1·399 g.) was dissolved in water (250 c.c.) containing potassium chloride (5 g.) and shaken for 8 days at 17° with sodium periodate (50 c.c.; 0·236M). At the end of this time titration showed that periodate equivalent to 125·6 c.c. of 0·1N-arsenite had been used in oxidising the gum.

In a similar experiment the gum (0·504 g.) required for oxidation periodate equivalent to 47·0 c.c. of 0·1N-arsenite. If, as indicated above, the gum contains four mols. of pentose, three mols. of hexose and one mol. of uronic acid per repeating unit of equivalent 1190, these figures show that an average of 1·07 mol. of formic acid is produced and an average of 5·2 mols. of periodate are consumed per repeating unit.

(*c*) The gum (0·5 g.) was oxidised in the usual manner for 200 hours. The solution was then cooled to 0° and filtered from potassium periodate. Slight excess of a solution of barium chloride was then added, and the precipitated barium iodate and periodate filtered off. The last traces of periodate and iodate were destroyed by bubbling sulphur dioxide through the filtrate which was then concentrated in a vacuum to a dry solid. A furfuraldehyde determination was then carried out in the usual manner.

In a second experiment the gum (0·5 g.) was oxidised as described above and the salts were then removed by dialysis [Found: Furfuraldehyde, 10·0 and 11·6. Calc. (for the loss of two pentose units and one uronic acid unit by periodate oxidation), 10·9; (for the loss of two pentose units only), 14·6%].

Hydrolysis of the oxidised gum. The oxidised gum (2·864 g.; see above for preparation) was hydrolysed by boiling with N-sulphuric acid (50 c.c.) for 48 hours. Since the solution became very dark and since the polysaccharide did not completely dissolve it was not possible to tell when the hydrolysis was completed. Sulphuric acid was precipitated by the addition of barium hydroxide, and the solution, after filtration, was concentrated in a partial vacuum to a solid. This residue was extracted exhaustively with methanol, and the extracts were concentrated under diminished pressure, to a syrup which was made up to 10 c.c. with water.

A galactose estimation on the solution (4 c.c.) gave 387 mg. of phenylmethylhydrazone, m. p. 186°. This is equivalent to approximately 1·5 mols. of galactose (per repeating unit of equiv. 1220) in the oxidised gum.

An arabinose estimation on the solution (2 c.c.) gave *l*-arabinose benzoylhydrazone (20 mg.), m. p. 180° (decomp.), equivalent to 33 mg. of *l*-arabinose, corresponding to 0·5 mol. of *l*-arabinose residues (per repeating unit of equiv. 1200) in the oxidised gum. This value is certainly low owing to the conversion of arabinose into furfuraldehyde during the hydrolysis, and the true figure is probably nearer one mol.

No xylose could be detected (as the dibenzylidene dimethyl acetal, Breddy and Jones, *J.*, 1945, 738).

Estimation of $-CH_2 \cdot OH$ *Groups in the Gum.* (Method of Lindstedt, *Arkiv Kemi, Min. Geol.*, 1945, **20** *A*, No. 13.)—The gum (1·65 g.) was suspended in pyridine (30 c.c.) and triphenylmethyl chloride (5 g.) added, and the mixture heated on a water-bath at 100° for 12 hours. The mixture was then poured into cold water (200 c.c.) and the product filtered off and washed with alcohol and ether. The last traces of triphenylmethylcarbinol were removed by exhaustive extraction with alcohol and the product dried in a vacuum (yield 2·46 g.).

This product was shaken with concentrated sulphuric acid (10 c.c.) for 12 hours. The resultant thick black solution was poured into water and the crude triphenylmethylcarbinol filtered off, washed with water and dilute ammonia, and weighed. The weight of pure triphenylmethylcarbinol was then obtained by exhaustive extraction from the filtered solid with alcohol (Found: 1·05 g. A polysaccharide containing four primary alcohol groups per repeating unit of 1220 requires 1·04 g.).

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