126. *The Constitution of Cherry Gum. Part I. Composition.*

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The similarity of cherry gum (from two sources) and damson gum (Hirst and Jones, J., 1938, 1174) is indicated by the identity of their products of hydrolysis and of the *d*-β-glycuronosido-2-*d*-mannose obtained on hydrolysis of the arabinose-free polysaccharides. Cherry gum contains also a small quantity (*ca.* 1·5%) of *d*-xylose.

Cherry gum collected in Arizona from wild cherry trees has been examined by Butler and Cretcher (*J. Amer. Chem. Soc.*, 1931, **53**, 4161), who came to the conclusion that it was a

polysaccharide having an equivalent weight 1791 and consisting of *l*-arabinose (8 mols.), *d*-xylose (6 mols.), *d*-galactose (6 mols.), *d*-mannose (3 mols.), and *d*-glycuronic acid (2 mols.).

The gum examined in the present research was obtained from cherry trees from two sources, and is fundamentally different from that described by the American authors. It appears to be essentially a homogeneous chemical entity having an equivalent weight of *ca.* 1450 and $[\alpha]_D^{20°}$ — 28° (as sodium salt in water. See Table I). It is exuded on the bark of the tree as a brownish, semi-solid mass, similar in appearance to damson gum, and is the neutral salt of an acidic polysaccharide, which can be transformed readily into a crisp white ash-free powder by precipitation from an acidified aqueous solution by addition of alcohol. In appearance and properties the substance is a typical gum, resembling gum arabic and damson gum in the viscosity of its aqueous solutions. Extraction with 70% alcohol failed to separate a polysaccharide differing in physical properties from the initial material. This is the usual method for the extraction of araban (Hirst and Jones, J., 1938, 496). The analytical figures for uronic anhydride and furfural indicate that there are present respectively 11·9% of uronic anhydride and 57·0% of pentosan.

The pentose obtained on hydrolysis was almost exclusively *l*-arabinose, and the uronic acid was *d*-glycuronic acid. *d*-Galactose and *d*-mannose were present and there was also a small amount of *d*-xylose. The *l*-arabinose appears to be combined in the furanose form, since its rate of hydrolysis is the same as that of the *l*-arabinose in the damson gum molecule, which is known to be of the furanose type. The aldobionic acid of cherry gum is identical with that of damson gum, the proof of its structure being made on the lines described by Hirst and Jones (J., 1938, 1175). A quantitative estimation indicated that in the original polysaccharide the various sugars were combined in the following proportions: glycuronic acid (1 mol.), galactose (2 mols.), mannose (1 mol.), and arabinose (6 mols.). The gum also contains a small amount (*ca.* 1·5%) of *d*-xylose: it is improbable that this is produced by decarboxylation of the glycuronic acid during hydrolysis. Should it prove to be the case that *d*-xylose is an essential part of the molecule, the molecular weight of the polysaccharide must be at least 7500.

Experimental.

Purification of Cherry Gum.—The gum, which resembled damson gum in properties, was converted into the acidic polysaccharide by precipitation with alcohol from aqueous solutions to which dilute hydrochloric acid had been added (for further details, see Hirst and Jones, J., 1938, 1177). The acidic gum did not dissolve so readily in warm water as that from damson gum, but otherwise resembled it in properties (soluble thallium salt; insoluble thallium complex; no insoluble copper complex; no reduction of Fehling's solution).

Table I.

Sample No.	Equiv. wt.*	$[\alpha]_D^{20°}$.†	Source.
1	1503	— 28·0°	North of England.
2	1420	— 26·0	Somerset.
3	1450	— 27·0	After extraction of (1) by 70% alcohol.

* By titration with N/10-sodium hydroxide.
† As sodium salt in water (*c*, 1·0).

The work described below was carried out with sample (1).

The purified gum had a small iodine number (1·0 g. required 2·5 c.c. of N/10-iodine). This small value is probably not significant, since the gum had a small ethoxyl content (2·0%, probably due to esterification during the purification process) [Found: OMe content of crude gum, nil; N, 0·2% (probably due to the presence of a small amount of protein); furfural (purified gum), 31·8%, estimated as phloroglucide after treatment of the polysaccharide with boiling 12% hydrochloric acid. Methyl pentose appeared to be absent. Uronic acid anhydride content calculated from the amount of carbon dioxide evolved on boiling with 12% hydrochloric acid, 11·9%]. (A substance containing 11·9% of uronic anhydride and no other acidic residues should have an equivalent weight of 1479. Found by titration of the gum with alkali, 1503). This proportion of uronic anhydride accounts for 3·0% of the total furfural (for factors

used in this and other analyses, see Hirst and Jones, *loc. cit.*, p. 1177), leaving 28·8% of furfural contributed by the pentosan portion of the polysaccharide, and since the major portion of the pentose present is *l*-arabinose (see below), the calculated anhydroarabinose content of the gum is 54·1% [Found: 52·0% (from direct estimation of arabinose after hydrolysis. See below). Anhydrogalactose (estimated after oxidation to mucic acid, 18·0%. For factor used, see below].

Graded Hydrolysis of Cherry Gum.—(a) Cherry gum (45 g.) was heated with water (1 l.) at 90—95°, the acidity of the solution being sufficient to bring about slow graded hydrolysis (compare damson gum, *loc. cit.*); the reaction was followed by polarimetric and iodometric observations: $[\alpha]_D^{20°}$ − 28° (*c*, 0·45 in water) (initial value); + 7·0° (6⅓ hrs.); + 20·0° (10¼ hrs.); + 50·0° (22½ hrs.); + 58·0° (27 hrs.); + 62° (34 hrs.); + 65° (45½ hrs.). A much slower hydrolysis continued beyond this stage. The increase in iodine titre was followed by titration of 2 c.c. portions of the solution with N/10-iodine by Baker and Hulton's method (*Biochem. J.*, 1920, **14**, 754): initial value (in c.c. of N/10-iodine, calculated for 1 g. of cherry gum), 2·5 c.c.; 9·3 (1⅔ hrs.); 17·8 (3 hrs.); 30 (6⅓ hrs.); 43·3 (10¼ hrs.); 63·3 (22½ hrs.); 73·0 (30½ hrs.); 77·2 (34 hrs.); 82·2 (45½ hrs.). The cooled solution was concentrated at 40°/12 mm. to 200 c.c. and poured into alcohol (1½ l.); it then gave an alcohol-insoluble polysaccharide (A) (14·0 g.), which was washed with alcohol (for purification, see below).

(b) *Reducing sugars obtained by graded hydrolysis.* The filtrate from (A) on concentration gave crystalline *l*-arabinose (19·5 g.), m.p. 160°, $[\alpha]_D^{20°}$ + 101° (*c*, 3·1 in water, equilibrium value). The mother-liquor was acid to Congo-red; it was neutralised with barium carbonate, filtered, and poured into alcohol, giving an insoluble barium salt (B) (5·1 g.) which appeared to be the barium salt of polysaccharide (A), which had been incompletely precipitated. The filtrate from (B) on concentration under reduced pressure gave a syrup (8·0 g.). An iodometric estimation of this syrup by Baker and Hulton's method showed the presence of a total amount of reducing sugar equivalent to 784 c.c. of N/10-iodine (equiv. to 7·07 g. of hexose or 5·88 g. of pentose). Some oligosaccharide was present at this stage, since the syrup underwent further hydrolysis with N/10-sulphuric acid. $[\alpha]_D^{21°}$ + 70° (initial value, *c* 4·0 in N/10-sulphuric acid), rising to $[\alpha]_D^{21°}$ + 91° (7 hrs., constant value). The iodine titre then indicated the presence of an amount of reducing sugar equivalent to 1000 c.c. of N/10-iodine (9·0 g. of hexose or 7·5 g. of pentose). Furfural determinations now showed the presence of 6·90 g. of pentose (calculated as *l*-arabinose). Oxidation of a portion of the solution with nitric acid under standard conditions gave mucic acid equivalent to the presence of a total amount of 0·56 g. of galactose. The solution contained *l*-arabinose (6·00 g.), estimated as *l*-arabinose diphenylhydrazone. Xylose appeared to be absent, since no cadmium bromide–cadmium xylonate double salt could be detected on oxidation of a portion of the above hydrolysis solution with bromine in the presence of cadmium carbonate. Since a portion of the hydrolysis solution on standing with phenylhydrazine gave no mannose phenylhydrazone, it was concluded that mannose was probably absent from this solution. A polysaccharide of equivalent weight 1454 and containing six molecules of arabinose would yield 63·2% of arabinose on hydrolysis (Found: 59·4%).

(c) *Polysaccharide (A).* Polysaccharide (A) (14·0 g.) was dissolved in N/10-hydrochloric acid (100 c.c.), filtered through kieselguhr, reprecipitated in absolute alcohol, washed free from mineral acid, and dried at 40°/12 mm. This treatment did not remove a small amount of absorbed protein. The cream-coloured powder obtained was easily soluble in water, giving a brown solution with an acid reaction to Congo-red. It gave no colour with aqueous iodine. $[\alpha]_D^{20°}$ + 32·2° (*c*, 1·6 in water). Uronic anhydride, 27·5% (calculated from the amount of carbon dioxide evolved on boiling with 12% hydrochloric acid). Furfural, 7·0% (estimated as phloroglucide after boiling with 12% hydrochloric acid under the standard conditions). The polysaccharide, on heating with nitric acid (*d* 1·2), gave mucic acid in a yield of 25·0%, corresponding to 40·3% of anhydrogalactose. The equivalent weight (by titration with N/10-sodium hydroxide in the cold) was 627. On titration with alkaline iodine by the method of Bergmann and Machemer, 1 g. of polysaccharide (A) required 7·0 c.c. of N/10-iodine, but this result is probably of no significance (see above). Found: OEt, 3·4%. A polysaccharide containing a repeating unit of 1 mol. of *d*-glycuronic acid, 1 mol. of *d*-mannose, and 2 mols. of *d*-galactose would have an equivalent weight of 662, would contain 48·9% of anhydrogalactose and 26·6% of uronic acid anhydride, and on distillation with 12% hydrochloric acid would give 6·7% of furfural.

(d) *Barium salt (B).* This was a white powder, easily soluble in water, giving a colourless, neutral solution. It gave no colour with aqueous iodine and had $[\alpha]_D^{20°}$ + 12·5° (*c*, 1·6 in water). Uronic anhydride, 23·0% (calculated from the amount of carbon dioxide evolved on boiling with 12% hydrochloric acid). Furfural, 6·0% (estimated as phloroglucide after boiling with 12% hydrochloric acid under the standard conditions). The polysaccharide, on heating with

nitric acid (*d* 1·2), gave mucic acid in a yield of 24·4%, corresponding to 39·0% of anhydrogalactose. On titration with alkaline iodine, 1 g. of polysaccharide required 27·0 c.c. of N/10-iodine, equivalent to a molecular weight of 758. The polysaccharide contained 9·1% of barium, indicating an equivalent weight of 753. A barium salt containing a repeating unit of 1 mol. of *d*-glycuronic acid, 1 mol. of *d*-mannose, and 2 mols. of *d*-galactose would have an equivalent weight of 730, would contain 44·4% of anhydrogalactose, 24·1% of uronic acid anhydride, and 9·7% of barium, and on distillation with 12% hydrochloric acid would give 5·3% of furfural.

(e) *Reducing sugars obtained on hydrolysis of polysaccharide* (*A*). The polysaccharide (A) (9·5 g.) was boiled with N-sulphuric acid (250 c.c.) for 4¼ hrs., the reaction being followed by iodometric and polarimetric observations. $[\alpha]_D^{20°}$ fell from + 32·0° to + 26·0° (*c*, 3·8 in N-sulphuric acid). The increase in iodine titre was followed by titration of 1 c.c. portions of the solution with N/10-iodine by Baker and Hulton's method: initial value (in c.c. of N/10-iodine calculated for 1 g. of polysaccharide A), 2·0; 53·0 (⅚ hr.); 87·0 (1¾ hrs.); 88·3 (2¾ hrs.); 103·0 (4¼ hrs.), followed by a slow upward rise in iodine titre. At the end of 4 hrs. a small quantity of dark brown protein material had separated. The cooled solution was neutralised with barium carbonate, filtered, and poured into alcohol. The precipitated barium salt (C) (5·7 g.) was washed with methyl alcohol and dried. Concentration of the methyl alcohol gave a syrup (4·2 g.) which crystallised. On trituration with alcohol, crystalline *d*-galactose (3·4 g.) was obtained, m. p. 162—163°. $[\alpha]_D^{20°}$ + 79·8° (*c*, 1·04 in water, equilibrium value). The syrup, after removal of *d*-galactose, still contained some *d*-galactose (0·27 g.), estimated as mucic acid after oxidation with nitric acid (*d* 1·2). In addition, it contained some *d*-mannose (0·28 g.), estimated as *d*-mannose phenylhydrazone (for factor used, see Hirst and Jones, J., 1938, 1179), m.p. 193°, $[\alpha]_D^{20°}$ + 22·8° (*c*, 0·5 in pyridine). Furfural determinations on the non-crystalline syrup indicated the presence of pentose (0·33 g.), and iodometric determinations by Baker and Hulton's method showed the presence of reducing sugars equivalent to 108 c.c. of N/10-iodine. Oxidation of a portion of the syrup with bromine in the presence of cadmium carbonate gave the characteristic cadmium bromide–cadmium xylonate, proving the presence of xylose. Arabinose appeared to be absent, since no arabinose diphenylhydrazone could be isolated. Since hexoses (0·55 g.) are equivalent to 61 c.c. of N/10-iodine and pentoses (0·33 g.) to 44·0 c.c. of N/10-iodine, making a total of 105 c.c., it would appear that *d*-mannose (0·28 g.), *d*-galactose (0·27 g.), and *d*-xylose (0·33 g.) were the only sugars present (Found: 108 c.c.). $[\alpha]_D^{20°}$ + 33·4° (*c*, 8·8 in water). A mixture of *d*-mannose, *d*-galactose, and *d*-xylose in the above proportions requires $[\alpha]_D^{20°}$ + 35·9°.

(f) *Hydrolysis of barium salt* (*B*). The barium salt (3·4 g.) was hydrolysed with N-sulphuric acid (50 c.c.) at 90—95°, the reaction being followed by polarimetric and iodometric observations: $[\alpha]_D^{20°}$ + 14·1° (*c*, 6·8 in N-sulphuric acid, initial value); + 25·3° (1 hr.); + 31·2° (3 hrs.); + 32·3° (4¼ hrs.). The increase in reducing power was followed by Baker and Hulton's method (*loc. cit.*): initial value (in c.c. of N/10-iodine per 1 g. of barium salt), 28·0; 51·4 (1·0 hr.); 63·2 (3 hrs.); 64·0 (4¼ hrs.). The solution was then neutralised with barium carbonate, filtered, and poured into absolute alcohol. The precipitated barium salt (1·7 g.) was washed with alcohol and dried. The filtrate on concentration gave *d*-galactose (1·3 g.), estimated as *d*-galactose phenylmethylhydrazone, m. p. and mixed m. p. 189°, and as mucic acid. The sugars, which had $[\alpha]_D^{20°}$ + 76·0° (*c*, 1·2, in water), also contained *d*-mannose (a trace); no other sugars could be detected.

The barium salt (1·7 g.) had $[\alpha]_D^{20°}$ − 1·0° (*c*, 0·82 in water). (Found: Ba, estimated as carbonate, 18·5%. The barium salt of an aldobionate requires Ba, 16·2%). Oxidation with nitric acid (*d* 1·2) under the standard conditions gave no mucic acid, showing the absence of galactose and galacturonic acid. This barium salt was a mixture of barium *d*-glycuronate and the barium salt of *d*-β-glycuronosido-*d*-mannose, since on hydrolysis with 2N-sulphuric acid it gave *d*-mannose (isolated as the phenylhydrazone) and *d*-glycuronic acid (isolated as its barium salt), $[\alpha]_D^{20°}$ + 15° in water (*c*, 1·1), and identified as the characteristic yellow crystalline solid formed on heating the barium salt with *p*-bromophenylhydrazine acetate.

(g) *Aldobionic acid from polysaccharide A.* The precipitated barium salts (C) consisted of the barium salt of β-*d*-glycuronosido-2-*d*-mannose mixed with a little material which still contained galactose. $[\alpha]_D^{20°}$ − 19·7° (*c*, 0·94 in water) (Found: furfural, 11·5; Ba, estimated as barium carbonate, 15·6. The barium salt of β-*d*-glycuronosido-2-*d*-mannose requires furfural, 10·1; Ba, 16·2%). Oxidation with nitric acid under the standard conditions gave mucic acid equivalent to the presence of 2·5% of galactose.

The barium aldobionate (0·73 g.) was very resistant to hydrolysis, but its partial cleavage could be effected with N-hydrochloric acid (25 c.c.) for 23 hrs. $[\alpha]_D^{20°}$ − 17° (initial value, *c*, 2·8); + 10° (16 hrs.); the solution then became too dark for further observation. Iodine

titre (in c.c. of N/10-iodine per 1 g. of aldobionate): 0·86 (initial value); 1·36 (2 hrs.); 2·25 (6⅓ hrs.); 2·52 (11 hrs.); 3·62 (18 hrs.); 2·80 c.c. (23 hrs.) (decomposition of the sugars had begun). The cooled solution, when neutralised with silver carbonate, filtered, and poured into alcohol, gave an insoluble barium salt (0·60 g.). The alcoholic filtrate on concentration gave a syrup (0·13 g.), $[\alpha]_D^{20°}$ + 42·7° (*c*, 1·3 in water), which consisted of *d*-mannose (0·07 g.), isolated as *d*-mannose phenylhydrazone, m. p. and mixed m. p. 196°, and *d*-galactose (0·06 g.), estimated as mucic acid. The filtrate from mannose phenylhydrazone, on heating with an excess of phenylhydrazine acetate, gave *d*-galactosazone, m. p. 200° (characteristic crystalline shape). The barium salts (0·60 g.), $[\alpha]_D^{20°}$ + 3° (*c*, 3·8 in water), on further hydrolysis with 2N-sulphuric acid (15 c.c.) at 90—95° during 20 hrs., gave *d*-mannose (0·15 g., estimated as the phenylhydrazone) and barium *d*-glycuronate (0·20 g.), $[\alpha]_D^{20°}$ + 16·9° (*c*, 1·0 in water), identified as the characteristic yellow derivative formed on heating with *p*-bromophenylhydrazine acetate.

Summary of Results. Composition of Cherry Gum.—The above results indicate that the sugar residues in cherry gum were combined in the proportions indicated: *l*-arabinose (6 mols.), *d*-galactose (2 mols.), *d*-mannose (1 mol.), and *d*-glycuronic acid (1 mol.). The gum also contains a small amount of *d*-xylose.

TABLE II.

	Uronic anhydride.	Furfural.	Arabinose residues, calculated as $C_5H_8O_4$.	Galactose residues, calculated as $C_6H_{10}O_5$.	Xylose residues, calculated as $C_5H_8O_4$.	Mannose residues, calculated as $C_6H_{10}O_5$.	Equiv. wt.
Calc. %	12·1	30·3	54·1	22·3	—	11·2	1454
Obs. %	11·9	31·8	52·0 [1] 54·0 [2]	18·0 [3] 18·0 [4]	*ca.* 1·2	8·0 [5]	1503

[1] From yield of arabinose and its diphenylhydrazone. [2] Estimated from yields of carbon dioxide and furfural. [3] Based on sum of galactose eliminated during formation of polysaccharide (A) and galactose present in polysaccharide (A), the factor 1·6 being used in mucic acid estimations. Owing to uncertainty as to the value of this factor, the galactan figures are approximate only. [4] Estimated from yield of mucic acid isolated from the oxidation of cherry gum with nitric acid (*d* 1·2). [5] Estimated from yields of *d*-mannose phenylhydrazone.

The arabinose-free polysaccharide (A) contains *d*-galactose (2 mols.), *d*-mannose (1 mol.), *d*-glycuronic acid (1 mol.), and *d*-xylose (*ca.* 3·0%).

TABLE III.

	Uronic anhydride.	Furfural.	Galactose residues, estimated as $C_6H_{10}O_5$.	Xylose residues, estimated as $C_5H_8O_4$.	Equiv. wt.	Mannose residues estimated as $C_6H_{10}O_5$.	$[\alpha]_D^{20°}$.
Calc. % [5]	25·5	8·5	47·0	—	690	23·5	—
Obs. % [1]	27·5	7·0	40·3	3·1 [3]	627	18·1 [6]	+ 32°
Obs. % [2]	24·2	7·3	43·7	3·0 [4]	645	19·5 [6]	+ 29

[1] Polysaccharide (A) from cherry gum. [2] Polysaccharide (A) from damson gum (Hirst and Jones, *loc. cit.*). [3] From yields of furfural. [4] From yield of 2 : 3 : 4-trimethyl *d*-xylose. [5] Assuming the presence of 3% anhydroxylose. [6] Estimated as mannose phenylhydrazone.

Methyl Heptamethyl Aldobionate.—The mixed barium salts (C) (3·60 g.) were dissolved in water (20 c.c.), and excess of thallous carbonate (1·4 g.) added. The precipitated barium carbonate was removed, the filtrate, to which was added N-thallous hydroxide (60 c.c.), evaporated to dryness at 40°/12 mm., and the finely powdered solid refluxed with an excess of methyl iodide (30 c.c.) during 24 hours. Excess of methyl iodide was removed by distillation, and the thallous iodide exhaustively extracted with acetone. Removal of the acetone gave a syrup (2·68 g., $n_D^{20°}$ 1·4682), which was further methylated by means of silver oxide and methyl iodide (yield, 2·63 g.), $n_D^{19°}$ 1·4695 (Found: OMe, 52·0%). The product on distillation gave (a) 0·25 g. of a mixture containing tetramethyl *d*-glycuronate, b. p. 140—170°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4540 (Found: OMe, 55·6%), (b) methyl heptamethyl aldobionate (1·46 g.) as a viscid liquid, b.p. 175—200°/0·001 mm. (bath temp.), $n_D^{20°}$ 1·4695, $[\alpha]_D^{20°}$ — 40·6° (*c*, 0·74 in water) (Found: OMe, 50·8; equiv. wt., by quantitative hydrolysis, 482. Calculated for $C_{20}H_{36}O_{12}$: OMe, 53·0%; equiv. wt., 468). Hydrolysis of the methyl heptamethyl aldobionate (0·86 g.) was effected by heating its solution in 7% hydrochloric acid at 90—95° for 5 hrs.: $[\alpha]_D^{21°}$ — 38·4° (initial value; *c*, 2·9); — 8·4° (¾ hr.); + 6·3° (1½ hrs.); + 16·1° (2¾ hrs.); + 30·0° (4½ hrs.); further polarimetric observations were impossible owing to darkening of the solution due to

slight decomposition. The solution was neutralised with silver carbonate, freed from silver with hydrogen sulphide, aerated, and neutralised with barium carbonate. The resulting solution, containing barium 2 : 3 : 4-trimethyl *d*-glycuronate and 3 : 4 : 6-trimethyl *d*-mannose, was evaporated to dryness, and the residue exhaustively extracted with ether. The ethereal solution on concentration gave 3 : 4 : 6-trimethyl *d*-mannose as a syrup (0·30 g.), $n_D^{19°}$ 1·4700, which crystallised; $[\alpha]_D^{20°}$ + 8·8° in water (*c*, 3·26) (Found : OMe, 40·3. Calc. for $C_9H_{18}O_6$: OMe, 41·8%). After recrystallisation from ether, its m. p. and mixed m. p. with an authentic sample were in agreement with the value (101°) previously recorded (Bott, Haworth, and Hirst, J., 1930, 1395).

The sugar (0·16 g.) was oxidised with bromine water at 40° for 6 hours, the solution being then neutralised with silver carbonate and filtered, and the silver removed as sulphide. On evaporation of the solvent, 3 : 4 : 6-trimethyl mannonolactone (0·13 g.) was obtained. This was distilled, giving an oil (0·11 g.), b. p. 160°/0·001 mm. (bath temp.), which crystallised on scratching. After recrystallisation from ether, the pure lactone was obtained in plates, m. p. 98°, undepressed by authentic 3 : 4 : 6-trimethyl *d*-mannonolactone. The two lactones were shown to be identical by *X*-ray analysis. $[\alpha]_D^{17°}$ + 167° (initial value in water, *c*, 2·2), falling to + 110° (30 hrs., constant value, micro-polarimeter tube). The lactone on solution in liquid ammonia gave the corresponding 3 : 4 : 6-trimethyl *d*-mannonamide, m. p. (after recrystallisation from acetone) 142°, undepressed by an authentic specimen (Hirst and Jones, *loc. cit.*); $[\alpha]_D^{18°}$ + 23° (*c*, 0·6 in water, micro-polarimeter tube). It gave a strong positive Weerman reaction (yield of hydrazodicarbonamide, 75% of the theoretical, similar to that obtained with *d*-mannonamide).

2 : 3 : 4-*Trimethyl* d-*Glycuronic Acid*.—After removal of trimethyl mannose, the residual barium trimethyl glycuronate was dissolved in water and the solution, after acidification with N-sulphuric acid (2·0 c.c.), was filtered and evaporated to dryness under diminished pressure. The organic matter was extracted from the residue with boiling ether; the syrup (0·40 g.) obtained on removal of the ether had $n_D^{18°}$ 1·4710, $[\alpha]_D^{20°}$ + 52·4° in water (*c*, 0·44) (Found : OMe, 38·8; equiv. wt., 247. Calc. for trimethyl glycuronic acid : OMe, 39·4%; equiv. wt., 236). Oxidation of 2 : 3 : 4-trimethyl *d*-glycuronic acid (0·35 g.) with bromine water at 60° for 10 hours gave 2 : 3 : 4-trimethyl saccharic acid (0·32 g.), which was identified, after esterification with methyl-alcoholic hydrogen chloride, as the methyl ester of 2 : 3 : 4-trimethyl saccharolactone (0·28 g.), b. p. 140° (bath temp.)/0·002 mm., $n_D^{18°}$ 1·4600. This crystallised to a solid mass, $[\alpha]_D^{21°}$ + 100° (*c*, 1·1 in ethyl alcohol), m. p. 110° alone or admixed with an authentic specimen.

The author gratefully acknowledges his indebtedness to Prof. E. L. Hirst, F.R.S., for his interest and advice, to Dr. T. Malkin for the *X*-ray analyses, and to the Colston Research Society for a grant.

THE UNIVERSITY, BRISTOL. [*Received, January 12th*, 1939.]