100. *The Constitution of Damson Gum. Part III. Hydrolysis Products from Methylated Damson Gum.*

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Damson gum has been converted into its fully methylated derivative, which on hydrolysis gives 2 : 3 : 5-trimethyl *l*-arabinose (8 parts), 2 : 3-dimethyl *l*-arabinose (4 parts), 2 : 4 : 6-trimethyl *d*-galactose (3 parts), 2 : 4-dimethyl *d*-galactose (3 parts), 4(?)-methyl *d*-galactose (1 part), 2-methyl *d*-galactose (1 part), 2 : 3 : 4-trimethyl *d*-glycuronic acid (2 parts), and 2 : 3-dimethyl *d*-glycuronic acid (2 parts), in the approximate proportions indicated, together with unidentified derivatives of *d*-mannose and *d*-xylose.

It has been shown (Hirst and Jones, *J.*, 1938, 1174) that damson gum contains the following sugars in the proportions indicated : *d*-glycuronic acid (1 part), *d*-mannose (1 part), *d*-galactose (2 parts), *l*-arabinose (3 parts), and *d*-xylose (*ca.* 2%). The polysaccharide has now been converted into a homogeneous fully methylated derivative by the use of the thallium hydroxide method of methylation (compare Hirst and Jones, *J.*, 1938, 502).

Methylated damson gum underwent partial cleavage on boiling with 1% methyl alcoholic hydrogen chloride giving a material of lower molecular weight which, like part of the degraded methylated damson gum molecule (Hirst and Jones, *J.*, 1939, 1939, 1482), could be hydrolysed with difficulty on treatment with hot N-hydrochloric acid followed by boiling with 5% methyl alcoholic hydrogen chloride. Eight different sugar derivatives were recognised as hydrolysis products, namely, 2 : 3 : 5-trimethyl *l*-arabinose, 2 : 3-dimethyl *l*-arabinose, 2 : 4 : 6-trimethyl *d*-galactose, 2 : 4-dimethyl *d*-galactose, 2-methyl *d*-galactose, 4(?)-methyl *d*-galactose, 2 : 3 : 4-trimethyl *d*-glycuronic acid, and 2 : 3-dimethyl *d*-glycuronic acid. Derivatives of *d*-mannose and *d*-xylose must also be present, but the identity of these sugar derivatives is as yet uncertain.

In our earlier paper it was stated that the dimethyl galactose isolated from the hydrolysis of the methylated degraded gum was 4 : 6-dimethyl *d*-galactose. It has now been established beyond doubt that the major portion of the dimethyl *d*-galactose present in the hydrolysis products of methylated degraded damson gum and of methylated damson gum itself is in fact 2 : 4-dimethyl *d*-galactose (I) (Hirst, *J.*, 1942, 76). The melting points of 2 : 4-dimethyl α- and β-methylgalactosides and of the sugar anilide have been compared and found to be identical with authentic samples (kindly supplied by Dr. F. Smith of Birmingham University and by Dr. D. J. Bell of Cambridge University). In addition a sample of the amide of 2 : 4-dimethyl *d*-galactonic acid gave no depression on admixture with the amide prepared from an authentic sample of the sugar isolated

from damson gum. In contrast, the melting point of 4 : 6-dimethyl *d*-galactose (Bacon, Bell, and Lorber, *J.*, 1940, 147) was depressed on admixture with a specimen of our 2 : 4-dimethyl *d*-galactose. An independent proof of the structure of the 2 : 4-dimethyl *d*-galactose has been arrived at from a study of its degradation with periodic acid, which oxidised it to formaldehyde (II) and to αα′-dimethoxy-*l*-araboglutardialdehyde (III). This on further oxidation with bromine water gave the corresponding αα′-dimethoxy-β-hydroxy-*l*-araboglutaric acid recognised as its crystalline diamide (IV) (compare Smith, *J.*, 1939, 50). The 4 : 6-dimethyl *d*-galactose derivatives isolated from methylated degraded damson gum as described in the earlier paper must therefore have represented only a small portion of the total dimethyl galactose.

The proof of the identity of the other sugars depends upon the following facts :

(*a*) The 2 : 3 : 5-trimethyl *l*-arabinose was identified after oxidation as the well-characterised crystalline lactone and amide (Humphreys, Pryde, and Waters, *J.*, 1931, 1298).

(*b*) The 2 : 3-dimethyl *l*-arabinose was oxidised to 2 : 3-dimethyl *l*-arabonolactone which was recognised as the corresponding crystalline amide (Smith, *J.*, 1939, 753).

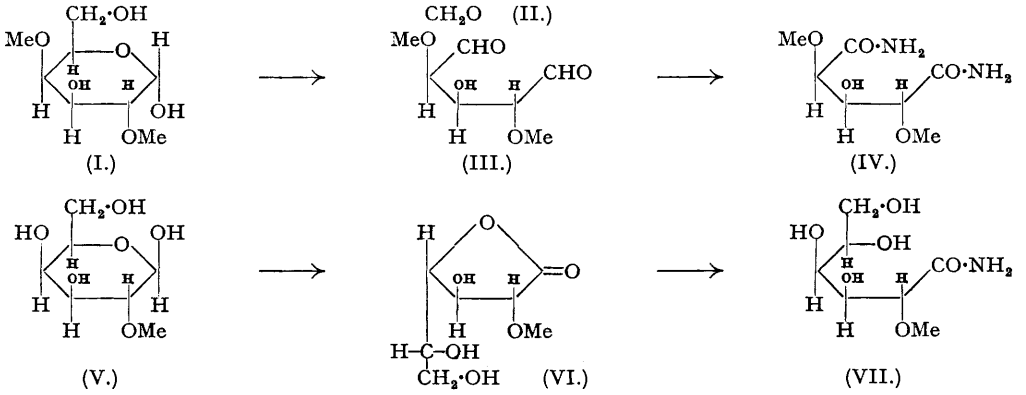
(*c*) Proof of the identity of the trimethyl *d*-galactose depended on the isolation of crystalline 2 : 4 : 6-trimethyl *d*-galactose and its crystalline anilide (Hirst and Jones, *J.*, 1939, 1486).

(*d*) 2-Methyl *d*-galactose (V) was recognised as the crystalline sugar and the corresponding anilide (compare Oldham and Bell, *J. Amer. Chem. Soc.*, 1938, **60**, 323; McCreath and Smith, *J.*, 1939, 390). On oxidation the sugar gave a *γ-lactone* (VI) showing the absence of a methoxyl on C_4. The corresponding *amide* (VII) gave a negative Weerman test showing the presence of a methoxyl group on C_2.

(*e*) 4(?)-*Methyl* d-*galactose* was characterised as the crystalline sugar, and its *anilide*. With phenylhydrazine the sugar gave without loss of methoxyl an *osazone* which appeared to be identical with 4-methyl *d*-galactosazone, while with methyl alcoholic hydrogen chloride the sugar showed no downward change of rotation indicating the presence of a methoxyl on C_4. Since the evidence available is not absolutely conclusive the conclusion that the sugar was 4-methyl *d*-galactose is given with reserve.

(*f*) Proof of the identity of 2 : 3 : 4-trimethyl *d*-glycuronic acid was furnished by its conversion to crystalline 2 : 3 : 4-trimethyl saccharic lactone methyl ester (Charlton, Haworth and Herbert, *J.*, 1931, 2855).

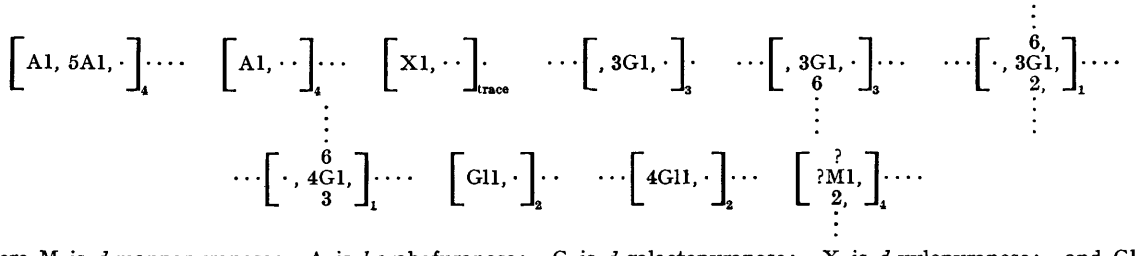
(*g*) The 2 : 3-dimethyl *d*-glycuronic acid was oxidised to 2 : 3-dimethyl *d*-saccharic acid which was identified as crystalline 2 : 3-dimethyl saccharic lactone methyl ester (Hirst and Jones, *J.*, 1939, 1482; Smith, *J.*, 1940, 1043).



The quantitative estimation of the sugars present after hydrolysis was not a simple matter owing to the number of substances involved and their similar properties. In particular it was not found possible to detect small quantities of xylose admixed with arabinose although some was known to be present. In addition, the hydrolysis of the mannose attached to the glycuronic acid molecule appeared to be attended by much decomposition of the mannose fraction and we have, therefore, been unable as yet to isolate the mannose derivative in a pure state. However, from an examination of methoxyl values and refractive indices and from the isolation of crystalline derivatives of the sugars it has been possible to obtain some idea of the relative proportions of the sugars present. The following figures are a provisional estimation of the approximate proportions of sugars formed on the hydrolysis of methylated damson gum : 2 : 3 : 5-trimethyl *l*-arabofuranose (8 parts), 2 : 3-dimethyl *l*-arabinose (4 parts), 2 : 4 : 6-trimethyl *d*-galactose (3 parts), 2 : 4-dimethyl *d*-galactose (3 parts), 2-methyl *d*-galactose (1 part), 4(?)-methyl *d*-galactose (1 part), 2 : 3 : 4-trimethyl *d*-glycuronic acid (2 parts), 2 : 3-dimethyl *d*-glycuronic acid (2 parts), methylated mannose, and methylated xylose. Previous work had shown that the methylated derivative of the " degraded," autohydrolysed, arabinose-free damson gum gave on hydrolysis : 2 : 3 : 4-trimethyl *d*-xylose, 2 : 3 : 4 : 6-tetramethyl *d*-galactose, 2 : 3 : 4-trimethyl *d*-galactose, 2 : 4 : 6-trimethyl *d*-galactose, 2 : 4-dimethyl *d*-galactose, 2 : 3 : 4-trimethyl *d*-glycuronic acid, 2 : 3-dimethyl *d*-glycuronic acid, and an unidentified derivative of *d*-mannose, with a trace of 4 : 6-dimethyl *d*-galactose. It will be observed from a comparison of these two sets of results that the 2 : 3 : 4 : 6-tetramethyl *d*-galactose and 2 : 3 : 4-trimethyl *d*-galactose do not occur among the hydrolysis products of methylated damson gum. It is inferred, therefore, that the arabinose molecules, which are probably all in the furanose form (compare

Hirst and Jones, *loc. cit.*), are attached to the galactose molecules which give rise to 2 : 3 : 4 : 6-tetramethyl *d*-galactose and 2 : 3 : 4-trimethyl *d*-galactose on hydrolysis of the methylated derivative of degraded damson gum. Since only *l*-arabinose is removed during the autohydrolysis of damson gum (Hirst and Jones, *loc. cit.*), and since hydrolysis of the methylated damson gum gave 2 : 3 : 5-trimethyl arabinose and 2 : 3-dimethyl arabinose in the ratio 2 to 1, it follows that there must be two side chains present in each repeating unit composed of arabinose (3 parts), galactose (2 parts), mannose (1 part), and glycuronic acid (1 part), and that these consist of *l*-arabinose only and are united to C_6 and C_3 of the galactose units in the main chain of the molecule. One side chain consists of one molecule of arabofuranose while the other consists of two molecules of *l*-arabofuranose linked to one another through C_1 and C_5, and the reducing group of the resulting disaccharide is united glycosidically to the main chain of the molecule. As the molecular proportions of 2 : 3 : 4-trimethyl and 2 : 3-dimethyl *d*-glycuronic acids appear to be constant in both the methylated degraded and methylated damson gums, it seems that they are not directly combined with any *l*-arabinose molecules. On the other hand, 2- and 4(?)-methyl *d*-galactoses present in the products of hydrolysis of methylated damson gum were not found among the sugars formed on hydrolysis of the methylated degraded gum; it appears, therefore, that the *l*-arabinose molecules are attached in some way to the sugars which give rise to monomethyl *d*-galactose on hydrolysis of the methylated gum. The possibility that the monomethyl *d*-galactoses result from incomplete methylation remains; we prefer to believe, however, that these monomethyl sugars are an integral part of the methylated gum molecule.

It is not possible at this stage to suggest any precise formula for damson gum since many points remain to be determined. For example, whether the polysaccharide is built up of a main chain of galactopyranose units linked alternately through carbon atoms 1, 3 and 1, 6, as seems to be fairly common in the galactose-containing polysaccharides, is as yet unknown. New experimental methods for the determination of the structure of the complex polysaccharides are being developed and by their use it is hoped to solve some of the outstanding problems encountered in this branch of carbohydrate chemistry. It is apparent, however, that the repeating unit of damson gum must be built up of the following residues, the precise order of arrangement being as yet undefined :



where M is *d*-mannopyranose; A is *l*-arabofuranose; G is *d*-galactopyranose; X is *d*-xylopyranose; and Gl is *d*-glycuronic acid.

Experimental.

(a) *Methylation of Damson Gum.*—The purified gum, $[\alpha]_D^{20°}$ — 26°, equiv. wt. 1100 (Hirst and Jones, *J.*, 1938, 1174), (50 g.) was suspended in water (300 c.c.) and brought into solution by the addition of N-thallous hydroxide solution (100 c.c.). An excess of N-thallous hydroxide solution (1½ l.) was evaporated to 300 c.c. in a silver dish and added to the solution of the thallium salt of the gum. The precipitated thallium complex (A) (200 g.) was filtered off, washed with alcohol, and dried. It was a white powder, sparingly soluble in water and containing 76% of thallium titratable with dilute sulphuric acid using phenolphthalein as an indicator. The dry finely powdered thallium complex was boiled in the dark with dry methyl iodide (500 c.c.) for 60 hours. Excess of methyl iodide was removed by distillation and the yellow solid (B) was exhaustively extracted with methyl alcohol. The extract on concentration gave a partially methylated gum, to which was added the filtrate from (A) together with N-thallous hydroxide (330 c.c.), and the mixture was evaporated to dryness at 40°/12 mm. with exclusion of carbon dioxide. The dry solid was finely powdered (120 mesh) and boiled with methyl iodide (300 c.c.). After 60 hours, excess of methyl iodide was removed by distillation and the solid residue exhaustively extracted with methyl alcohol. The alcoholic solution was concentrated to a syrup and dissolved in ethyl alcohol–benzene (200 c.c.). To the solution was added thallous ethoxide [prepared from N-thallous hydroxide (500 c.c.)] and the mixture evaporated to dryness. The powdered solid was boiled with methyl iodide (200 c.c.) as before and the product was isolated in the usual manner. One more treatment with thallous ethoxide, followed by methyl iodide, gave methylated damson gum (41·7 g.). A quantity of incompletely methylated polysaccharide (8·7 g.) was obtained when the solid (B) was extracted with water after the methyl alcoholic extraction.

Methylated damson gum is a white solid, soluble in cold water, benzene, acetone, chloroform, dioxan, *m*-cresol, and methyl alcohol; insoluble in hot water, light petroleum, and ether.

The methylated product (32 g.), OMe 41·5%, was fractionally precipitated from chloroform by means of light petroleum. Four fractions were isolated.

Fraction I. 0·5 g. $[\alpha]_D^{20°}$ — 40° (*c*, 0·57 in methyl alcohol). OMe, 40·3%.

Fraction II. 20·5 g. $[\alpha]_D^{20°}$ — 40° (*c*, 0·65 in methyl alcohol). OMe, 40·5%. $\eta_{sp.}/c$, 0·127 in *m*-cresol.

Fraction III. 5·0 g. $[\alpha]_D^{20°}$ — 39° (*c*, 0·75 in methyl alcohol). OMe, 40·0%. $\eta_{sp.}/c$, 0·108 in *m*-cresol.

Fraction IV. (Residue). 6·0 g. $[\alpha]_D^{20°}$ — 38° (*c*, 0·8 in methyl alcohol). OMe, 41·8%. $\eta_{sp.}/c$, 0·09 in *m*-cresol.

Fraction I contained impurities. Fractions II, III, and IV showed no significant differences and were combined. $[\alpha]_D^{20°}$ — 39° (*c*, 0·6 in methyl alcohol). Equiv. wt., 1410 (by titration with alkali). Uronic anhydride, 13·3% (from the carbon dioxide evolved on heating with 12% hydrochloric acid) (Found : C, 51·5; H, 7·5; OMe, 40·6%).

Partial Hydrolysis of Methylated Damson Gum.—Methylated damson gum (25 g.) was dissolved in 1% methyl alcoholic hydrogen chloride (500 c.c.) and heated under reflux. $[\alpha]_D^{20°}$ — 39° (*c*, 5·0 initial value), — 27° (2/3 hr.), — 12° (2¼ hrs.), — 5° (3¼ hrs.), + 13° (18¼ hrs.), + 13° (21 hrs.); (very little change of rotation on further heating). Hydrochloric acid

was removed with silver carbonate and the solution filtered. On removal of the methyl alcohol a viscid syrup (25·78 g.) was obtained. This was submitted to fractional distillation.

Fraction I. 2 : 3 : 5-Trimethyl methyl-*l*-arabinoside (4·94 g.), b. p. 98°/0·003 mm. (bath temp.), $n_D^{21°}$ 1·4375, OMe, 61·8%, $[\alpha]_D^{20°}$ − 66° (*c*, 0·77 in methyl alcohol).

Fraction II. Dimethyl methyl-*l*-arabinoside admixed with some 2 : 3 : 5-trimethyl methyl-*l*-arabinoside (0·6 g.), b. p. 135°/3·003 mm. (bath temp.), $n_D^{17°}$ 1·4520, OMe, 51·7%, $[\alpha]_D^{20°}$ − 5° (*c*, 0·6 in methyl alcohol).

Complete Hydrolysis of Methylated Damson Gum.—The still residue (20·2 g.), an orange viscid liquid, was dissolved in N-hydrochloric acid (400 c.c.) and heated on the boiling water-bath for 6 hours. (The solution became too dark for polarimetric observation. Some furfural was formed.) The solution was neutralised with silver carbonate, filtered, and the silver salts decomposed with hydrogen sulphide. Silver sulphide was removed by filtration, and the filtrate aerated to remove hydrogen sulphide, neutralised with barium carbonate, and filtered. By this means it was possible to obtain the barium salts of the methylated glycuronic acids, free from admixed barium chloride. The aqueous solution (C) was concentrated at 60°/12 mm. to a small volume (60 c.c.) and exhaustively extracted with benzene in an all-glass apparatus.

The benzene extract on concentration gave a syrup (7·90 g.) which was converted into the glycosides by boiling with 1% methyl alcoholic hydrogen chloride (100 c.c.) for 15 hours. Hydrochloric acid was removed with silver carbonate and the filtered solution concentrated at 760 mm. to a syrup (8·22 g., $n_D^{20°}$ 1·4518) which was fractionally distilled giving :

Fraction III. 2 : 3 : 5-Trimethyl methyl-*l*-arabinoside (3·21 g.), b. p. 100°/0·002 mm., $n_D^{21°}$ 1·4395, $[\alpha]_D^{20°}$ − 31° (*c*, 0·58 in methyl alcohol) (Found : OMe, 58·8. Calc. for $C_9H_{14}O_5$: OMe, 60·8%).

Fraction IV. Mainly dimethyl methyl-*l*-arabinoside (1·81 g.), b. p. 100—130°/0·002 mm., $n_D^{18°}$ 1·4508, $[\alpha]_D^{20°}$ − 7° (*c*, 0·39 in methyl alcohol) (Found : OMe, 49·2. Calc. for $C_8H_{16}O_5$: OMe, 48·4%).

Fraction V. Mainly 2 : 4 : 6-trimethyl methyl-*d*-galactoside (1·77 g.), b. p. 130—160°/0·002 mm., $n_D^{18°}$ 1·4580, $[\alpha]_D^{20°}$ + 36° (*c*, 0·52 in methyl alcohol) (Found : OMe, 50·0. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%).

Residue, 1·30 g. (D).

The aqueous solution (C) after extraction was concentrated under reduced pressure to a syrup which was exhaustively extracted with acetone, leaving the barium salts (E) (5·0 g.). Concentration of the acetone extract gave a syrup (8·80 g.) to which was added residue (D) and the whole was converted to the glycosides by boiling with 2% methyl alcoholic hydrogen chloride (100 c.c.) during 15 hours. Hydrochloric acid was removed with silver carbonate and the solution filtered. Concentration of the filtrate at 40°/12 mm. gave a syrup (9·8 g.). This was separated into two fractions by exhaustive extraction with ether : ether soluble (7·62 g.), $n_D^{20°}$ 1·4745; ether insoluble (1·9 g.), $n_D^{19°}$ 1·4830 (F). The ether soluble portion was fractionally distilled in a vacuum.

Fraction VI. 2 : 4 : 6-Trimethyl methyl-*d*-galactoside (1·71 g.), b. p. 126—135°/0·003 mm., $n_D^{19°}$ 1·4595, $[\alpha]_D^{20°}$ + 41° (*c*, 0·80 in methyl alcohol) (Found : OMe, 51·2. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%).

Fraction VII. 2 : 4-Dimethyl and 2 : 4 : 6-trimethyl methyl-*d*-galactosides (0·89 g.), b. p. 130—150°/0·002 mm., $n_D^{18°}$ 1·4720, $[\alpha]_D^{19°}$ + 55° (*c*, 0·47 in methyl alcohol) (Found : OMe, 45·5%).

Fraction VIII. 2 : 4-Dimethyl methyl-*d*-galactoside (2·85 g.), b. p. 150—160°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4770, $[\alpha]_D^{17°}$ + 78° (*c*, 0·51 in methyl alcohol) (Found : OMe, 40·9. Calc. for $C_9H_{18}O_6$: OMe, 41·9%).

To the still residue (2·19 g.) was added fraction (F) (1·9 g.) and the whole distilled from a flask without a fractionation column.

Fraction IX. 2 : 4-Dimethyl and monomethyl methyl-*d*-galactosides (1·25 g.), b. p. 151—166°/0·002 mm., $n_D^{19°}$ 1·4812, $[\alpha]_D^{19°}$ + 71° (*c*, 0·49 in methyl alcohol) (Found : OMe, 36·8. Calc. for $C_9H_{18}O_6$: OMe, 41·9%).

Fraction X. Monomethyl methyl-*d*-galactosides (2·15 g.), b. p. 166—210°/0·003 mm., $n_D^{19°}$ 1·4900, $[\alpha]_D^{20°}$ + 63° (*c*, 0·49 in methyl alcohol) (Found : OMe, 29·9. Calc. for $C_8H_{16}O_6$: OMe, 29·8%).

Residue, 0·54 g.

The barium salts (E) (5·0 g.) were dissolved in water and the barium exactly removed as sulphate by the addition of N-sulphuric acid (15·5 c.c.). The solution was spun on the centrifuge to remove barium sulphate, and concentrated under reduced pressure to a syrup which was boiled with 2% methyl alcoholic hydrogen chloride (200 c.c.) for 15 hours. Hydrochloric acid was removed with silver carbonate and the filtered solution concentrated to a syrup (3·27 g.) which was fractionally distilled in a vacuum.

Fraction XI. Methyl ester of 2 : 3 : 4-trimethyl methyl-*d*-glycuronide (0·92 g.), b. p. 140—150°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4510, $[\alpha]_D^{19°}$ 70° (*c*, 0·59 in methyl alcohol) (Found : Equiv. wt., 273; OMe, 54·0. Calc. for $C_{11}H_{20}O_7$: Equiv. wt., 264; OMe, 58·7%).

Fraction XII. Mainly methyl ester of dimethyl methyl-*d*-glycuronide (0·56 g.), b. p. 150—160°/0·001 mm. (bath temp.), $n_D^{18°}$ 1·4660, $[\alpha]_D^{19°}$ + 64° (*c*, 0·6 in methyl alcohol) (Found : OMe, 48·5. Calc. for $C_{10}H_{18}O_7$: OMe, 49·9%).

Residue, 1·74 g. This was boiled with 5% methyl alcoholic hydrogen chloride (30 c.c.) for 60 hours. Hydrochloric acid was removed with silver carbonate and the filtered solution concentrated at 40°/12 mm. and the residual syrup (1·5 g.) distilled in a vacuum.

Fraction XIII. Methyl ester of trimethyl methyl-*d*-glycuronide admixed with some dimethyl derivative (0·54 g.), b. p. 160—190°/0·001 mm. (bath temp.), $n_D^{23°}$ 1·4670, OMe, 53·0%. (The residue (0·9 g.) was discarded.)

Examination of the Various Fractions.—Fractions I and III (8·15 g.) were combined and a portion (6·29 g.) hydrolysed with N/2-hydrochloric acid (100 c.c.) on the boiling water-bath for 3 hours. $[\alpha]_D^{22°}$ − 50° (*c*, 6·29, initial value in N/2-hydrochloric acid); − 14° (¾ hour); − 11° (1½ hours); − 10° (2¾ hours) (constant value). This equilibrium value would be given by 6·46 g. of trimethyl methyl-*l*-arabofuranoside and 1·69 g. of dimethyl methyl-*l*-arabinoside in fractions I and III combined. Hydrochloric acid was removed with silver carbonate and the solution filtered; silver ions were removed with hydrogen sulphide and the filtered solution concentrated to a syrup under reduced pressure. The syrup (5·70 g.) was freed from a trace of silver sulphide by extraction with acetone, and fractionally distilled in a vacuum.

Fraction XIV. Trimethyl *l*-arabofuranose (4·10 g.), b. p. 120°/0·002 mm. (bath temp.), $n_D^{22°}$ 1·4485, $[\alpha]_D^{21°}$ − 30° (*c*, 4·0 in water) (Found : OMe, 48·6. Calc. for $C_8H_{16}O_5$: OMe, 48·4%).

Fraction XV. Trimethyl *l*-arabofuranose and 2 : 3-dimethyl *l*-arabinose (1·02 g.), b. p. 120—160°/0·002 mm. (bath temp.), $n_D^{21°}$ 1·4615, $[\alpha]_D^{21°}$ + 16·2° (*c*, 1·0 in water) (Found : OMe, 42·0. Calc. for $C_7H_{14}O_5$: OMe, 34·9%).

Residue, 0·28 g. (probably polymerised products). Loss during distillation, 0·32 g.

Oxidation of Fraction XIV.—This fraction (3·98 g.) was dissolved in water (20 c.c.), bromine added (5 c.c.), and the mixture heated on the water-bath at 48° for 4 hours and then at 20° for 15 hours. A further four hours at 40° gave a non-reducing solution. Bromine was removed by aeration and the solution neutralised with silver carbonate and filtered. The filtrate was treated with hydrogen sulphide, the solution filtered from silver sulphide, concentrated to a syrup (3·65 g.; $n_D^{20°}$ 1·4448), and fractionally distilled in a vacuum.

Fraction XVI. 2 : 3 : 5-Trimethyl *l*-arabonolactone (3·02 g.), b. p. 120°/0·002 mm. (bath temp.), $n_D^{20°}$ 1·4445 (supercooled liquid), $[\alpha]_D^{20°}$ − 43·0°, m. p. 30° (Found : OMe, 48·2; equiv. wt., 200. Calc. for $C_8H_{16}O_6$: OMe, 48·9%; equiv. wt., 190).

This fraction had all the constants of an authentic specimen of 2 : 3 : 5-trimethyl *l*-arabonolactone and on treatment with liquid ammonia gave 2 : 3 : 5-trimethyl *l*-arabonamide in quantitative yield. M. p. and mixed m. p. 136°, $[\alpha]_D^{20°}$ + 22° (*c*, 0·73 in ethyl alcohol).

Fraction XVII. 2 : 3 : 5-Trimethyl *l*-arabonolactone admixed with some dimethyl *l*-arabonolactone (0·42 g.), b. p. 120—130°/0·002 mm. (bath temp.), $n_D^{20°}$ 1·4550. This fraction was combined with Fraction XVIII(a) (see below).

Oxidation of Fraction XV.—0·99 G. was dissolved in water (10 c.c.) and bromine added (1·5 c.c.). The oxidation was carried out exactly as described for fraction XIV and gave a syrup (0·89 g.; $n_D^{21°}$ 1·4580) which was fractionally distilled in a vacuum.

Fraction XVIII(a). Dimethyl *l*-arabonolactone admixed with 2 : 3 : 5-trimethyl *l*-arabonolactone (0·42 g.), b. p. 121—138°/0·002 mm. (bath temp.), $n_D^{20°}$ 1·4555. This fraction was combined with Fraction XVII and the constants given below are for the mixture (0·84 g.). Equiv. wt., 182; $[\alpha]_D^{20°}$ − 20·5° (initial value in water, *c*, 0·94); − 19·5° (6½ hours); − 14·4° (70 hours) not constant (Found: OMe, 45·8%). On treatment with liquid ammonia, the lactone gave 2 : 3 : 5-trimethyl *l*-arabonamide, m. p. and mixed m. p. 137°. The residual non-crystalline amide gave a negative Weerman test indicating the absence of any amide with a hydroxyl group on C_2.

Fraction XVIII(b). Dimethyl *l*-arabonolactone (0·20 g.), b. p. 160°/0·002 mm. (bath temp.); $n_D^{20°}$ 1·4638; equiv. wt., 177; $[\alpha]_D^{20°}$ − 22·0° (initial value in water, *c*, 0·59); − 27·2° (5 hours); − 26° (22 hours); − 15·2° (70 hours; not constant) (Found: OMe, 37·5. Calc. for $C_7H_{12}O_5$: OMe, 35·2%). Solution in liquid ammonia, followed by evaporation of the solvent, gave crystals admixed with syrup. Trituration with acetone gave 2 : 3-dimethyl *l*-arabonamide (60 mg.), m. p. and mixed m. p. 160° (after recrystallisation from alcohol).

Fractions II and IV (2·33 g.) were dissolved in hydrochloric acid (100 c.c.) and heated on the boiling water-bath for 2 hours; $[\alpha]_D^{21°}$ − 5° (*c*, 2·33, initial value in N-hydrochloric acid); + 46° (2 hours, constant value). Hydrochloric acid was removed with silver carbonate and the filtered solution treated with hydrogen sulphide to remove any dissolved silver salts, and concentrated to a syrup (1·90 g.), $n_D^{20°}$ 1·4710, $[\alpha]_D^{20°}$ + 52° (*c*, 1·1 in water) (Found: OMe, 35·4%. Calc. for $C_7H_{14}O_5$: OMe, 34·9%). From the rotation of the free sugar (+ 52°) it can be calculated that this fraction contains 0·87 g. of trimethyl methyl-*l*-arabofuranoside and 1·50 g. dimethyl methyl-*l*-arabinoside.

The syrup (1·85 g.) was dissolved in water (10 c.c.) and bromine (3 c.c.) added. The oxidation product was worked up exactly as described for Fraction XIV, and gave a syrup (1·65 g.) which was fractionally distilled in a vacuum.

Fraction XIX. 2 : 3 : 5-Trimethyl *l*-arabonolactone (0·33 g.), b. p. 110°/0·001 mm. (bath temp.), $n_D^{19°}$ 1·4472, m. p. 27°, $[\alpha]_D^{21°}$ − 40° (*c*, 1·0, initial value in water) (Found: OMe, 48·4; equiv. wt., 198. Calc. for $C_8H_{14}O_5$: OMe, 48·9%; equiv. wt., 190). On treatment with liquid ammonia it gave the corresponding amide in quantitative yield, m. p. and mixed m. p. 137°; $[\alpha]_D^{20°}$ + 23° (*c*, 0·7 in ethyl alcohol).

Fraction XX. 2 : 3-Dimethyl *l*-arabonolactone (1·25 g.), b. p. 140—150°/0·001 mm. (bath temp.), $n_D^{23°}$ 1·4600 (Found: OMe, 38·3; equiv. wt., 188. Calc. for $C_7H_{12}O_5$: OMe, 35·2%; equiv. wt., 176), $[\alpha]_D^{21°}$ + 4° (*c*, 1·4, initial value in water); − 2° (1 hour); − 8° (5 hours); − 11° (7 hours); − 10° (24 hours); − 10° (74 hours). These rotation figures are in agreement with a mixture of 70% 2 : 3-dimethyl *l*-arabonolactone and 30% 2 : 4 : 6-trimethyl *d*-galactonolactone, or with a mixture of 2 : 3-dimethyl *l*-arabonolactone and some other dextro-rotatory dimethyl pentono-lactone.

Still residue. 0·20 G.; not further examined.

The lactone (1·20 g.) (Fraction XX) on treatment with liquid ammonia gave crystalline 2 : 3-dimethyl *l*-arabonamide, m. p. and mixed m. p. 159°, $[\alpha]_D^{21°}$ + 17° (*c*, 0·52 in water) (Found: OMe, 33·1. Calc. for $C_7H_{15}O_5N$: OMe, 32·1%). The residual amide (0·45 g.) could not be induced to crystallise. With sodium hypochlorite it gave sodium cyanate isolated as hydrazodicarbonamide. The yield indicated the presence of some 0·15 g. of an amide with a hydroxyl on C_2. From the above figures it is estimated from rotational data and from refractive index values that the total amount of 2 : 3-dimethyl *l*-arabinose present in fractions I, II, III, and IV was 2·81 g.

Fraction.	Weight (g.) as glucosides.	2 : 3 : 5-Trimethyl methyl -arabinoside.	2 : 3-Dimethyl methyl -arabinoside.	2 : 4 : 6-Trimethyl methyl	2 : 4-Dimethyl methyl -*d*-galactosides.	2-Methyl methyl	4(?)-Methyl methyl	2 : 3 : 4-Trimethyl methyl -glycuronosides.	2 : 3-Dimethyl methyl -glycuronosides.
I	4·94	6·46 [1]	1·69 [1]	—	—	—	—	—	—
III	3·21								
II	0·60	0·87 [2]	1·50 [2]	—	—	—	—	—	—
IV	1·81								
V	1·77	—	—	1·71 [3]	—	—	—	—	—
VI	1·71	—	—	1·44 [3]	—	—	—	—	—
VII	0·89	—	—	0·20	0·69 [3]	—	—	—	—
VIII	2·85	—	—	—	2·34 [3]	—	—	—	—
IX	1·25	—	—	—	0·92 [3]	0·16	0·16	—	—
X	2·15	—	—	—	0·10	1·0	1·0	—	—
XI	0·92	—	—	—	—	—	—	0·62	0·30
XII	0·56	—	—	—	—	—	—	0·46	0·64
XIII	0·53								
	23·20	7·33	3·19	3·35	4·05	1·16	1·16	1·08	0·94
Calculated yields of glycosides from 25 g. of polysaccharide:		7·86	3·67	2·36	4·23	1·19	1·99	2·50	2·38

[1] Fractions I and III combined. [2] Fractions II and IV combined. [3] From yield of anilide: for method of calculation see Part II.

Fraction V (1·77 g.). This fraction partially crystallised on distillation. The mixture of syrup and crystals was tiled; the syrup was absorbed, leaving crude 2 : 4 : 6-trimethyl β-methyl-*d*-galactoside (0·41 g.), m. p. 102°, $[\alpha]_D^{21°}$ + 18° (*c*, 0·34 in methyl alcohol) after recrystallisation from ether–light petroleum. When left in air the galactoside absorbed water giving the *hemihydrate*, m. p. 83—85° (Found: C, 48·9; H, 9·0; OMe, 50·7. $C_{10}H_{20}O_6,\frac{1}{2}H_2O$ requires C, 48·9; H, 8·6; OMe, 50·6%).

The glycoside (0·34 g.) was hydrolysed with N-hydrochloric acid (25 c.c.) on the boiling water-bath for 2¼ hours, $[\alpha]_D^{21°}$ + 72° (*c*, 1·38; equilibrium value). Hydrochloric acid was removed with silver carbonate and the filtered solution concentrated to a syrup which was dissolved in ether and filtered. Concentration of the syrup gave crystalline 2 : 4 : 6-trimethyl α-*d*-galactose, m. p. alone or on admixture with an authentic specimen, 105°, after recrystallisation from ether; $[\alpha]_D^{21°}$ + 122°, falling to + 86° in 24 hours (*c*, 1·2 in water) (Found: OMe, 42·3. Calc. for $C_9H_{18}O_6$: OMe, 41·9%).

The sugar (0·1 g.), on heating with aniline (0·2 c.c.) in ethyl alcohol (5 c.c.) during 5 hours and subsequent removal of the alcohol by distillation, gave 2 : 4 : 6-trimethyl *d*-galactose anilide, m. p. 179° (after recrystallisation from absolute

alcohol) (Found : C, 60·5; H, 7·35; N, 5·0. Calc. for $C_{15}H_{23}O_6N$: C, 60·5; H, 7·8; N, 4·7). The m. p. was not depressed by an authentic specimen prepared by Dr. E. G. V. Percival in the Edinburgh laboratories, but was depressed to 156° on admixture with a specimen of 2 : 3 : 4-trimethyl *d*-galactose anilide, m. p. 170°.

The sugar (0·2 g.) was dissolved in water (5 c.c.) and oxidised with bromine (1 c.c.) in the manner described above. The lactone (0·15 g.) was isolated as a syrup which was distilled in a vacuum, b. p. 160°/0·001 mm. (bath temp.); $n_D^{17°}$ 1·4700, $[\alpha]_D^{21°}$ + 143° (initial value in water, *c*, 0·46); + 117° (¾ hour); + 95° (2½ hours); + 69° (4½ hours); + 61° (8½ hours); + 52° (11 hours, constant value) (Found : equiv. wt., 222; OMe, 41·2. Calc. for $C_9H_{16}O_6$: equiv. wt., 220; OMe, 42·4%). The lactone on treatment with methyl alcoholic ammonia gave the crystalline amide in quantitative yield, m. p. 166° (after recrystallisation from acetone), $[\alpha]_D^{20°}$ + 73° (*c*, 0·72 in water). Treatment of the amide with sodium hypochlorite under the conditions described by Weerman gave no sodium cyanate showing the presence of the methoxyl group in position 2.

The syrup absorbed by the tile (1·36 g.) was extracted with ether and a portion of it (0·71 g.) was dissolved in N-hydrochloric acid (30 c.c.) and heated on the boiling water during 2½ hours; $[\alpha]_D^{21°}$ + 36° (*c*, 2·4, initial value); + 54° (1 hour); + 56° (2½ hours, constant value). Hydrochloric acid was removed by neutralising with silver carbonate and the solution filtered. Silver salts were removed from solution as silver sulphide and the solution concentrated to a syrup which was exhaustively extracted with acetone. The extracts on concentration gave a syrup (0·65 g.), $n_D^{22°}$ 1·4665; $[\alpha]_D^{20°}$ + 60° (*c*, 1·0 in water). In order to estimate the amount of 2 : 4 : 6-trimethyl *d*-galactose, the syrup (0·65 g.) was heated under reflux for 2 hours with alcohol (10 c.c.) containing aniline (1 c.c.). On removal of the alcohol by distillation the syrup crystallised. The anilide was triturated with alcohol–ether and filtered. Yield of anilide 0·40 g., m. p. 179°. The filtrate on concentration gave a further crop of crystals (0·20 g.). The total yield of anilide was thus 0·60 g. from 0·65 g. of sugar. The total yield of 2 : 4 : 6-trimethyl methyl-*d*-galactoside in this fraction was 1·71 g. No trace of 2 : 3 : 4-trimethyl *d*-galactose anilide could be detected. A mannose derivative may have been present in this fraction as the free sugar had a low rotation.

Fraction VI (1·71 g.). This fraction (1·45 g.) was dissolved in N-hydrochloric acid (40 c.c.) and heated on the boiling water-bath during 2½ hours; $[\alpha]_D^{20°}$ + 53° (*c*, 3·6, initial value in N-hydrochloric acid); + 76° (½ hour); + 70° (1½ hours); + 69° (2½ hours, constant value). The solution was neutralised with silver carbonate, filtered and the filtrate evaporated to a syrup (1·35 g.). $[\alpha]_D^{20°}$ + 73° (in water, *c*, 1·2). It did not crystallise on nucleation with 2 : 4 : 6-trimethyl *d*-galactose. The syrup was dissolved in alcohol (15 c.c.) containing aniline (2 c.c.) and heated under reflux during 2 hours. Alcohol was removed by distillation and the residual syrup nucleated with 2 : 4 : 6-trimethyl *d*-galactose anilide, when it crystallised. The crystals (0·90 g.) were triturated with ether and filtered. Concentration of the mother liquors gave a further crop of crystals (0·20 g.). Total yield (1·10 g.), m. p. 179° after recrystallisation from absolute alcohol. This corresponds to 1·44 g. of 2 : 4 : 6-trimethyl methyl-*d*-galactoside in this fraction; no other sugar could be detected.

Fraction VII (0·80 g.) was dissolved in N-hydrochloric acid (30 c.c.) and the solution heated on the boiling water-bath for 5½ hours. $[\alpha]_D^{22°}$ + 70° (initial value); + 73° (1½ hours); + 71° (3 hours); + 71° (5½ hours, constant value). Hydrochloric acid was removed by addition of silver carbonate and the filtered solution concentrated to a syrup (0·75 g.), $[\alpha]_D^{22°}$ + 76° (*c*, 2·0 in water), which did not crystallise. The syrup (0·70 g.) was dissolved in alcohol (10 c.c.) containing aniline (1 c.c.) and boiled for 2 hours. On removal of the solvent by distillation the residual syrup crystallised. The crystals (0·40 g.) were isolated after trituration with ether. M. p. and mixed m. p. with 2 : 4-dimethyl *d*-galactose anilide 207°. This corresponds to 0·69 g. of 2 : 4-dimethyl methyl-*d*-galactoside (calculated on the basis of a 50% yield of anilide; Hirst and Jones, *J.*, 1939, 1488).

Fraction VIII (2·85 g.) slowly crystallised. Crystal growth was accelerated by placing the syrup in an incubator at 50°. The syrup was triturated with acetone–ether and the resulting crystals of 2 : 4-dimethyl β-methylgalactoside (0·60 g.) were filtered off and washed with acetone–ether. M. p. 162°. $[\alpha]_D^{20°}$ + 5° (*c*, 1·0 in methyl alcohol) after recrystallisation from acetone (Found : C, 48·8; H, 8·1; OMe, 42·0. Calc. for $C_9H_{18}O_6$: C, 48·6; H, 8·2; OMe, 41·9%).

The crystals (0·5 g.) were dissolved in N-sulphuric acid (50 c.c.) and heated on the boiling water-bath for 5 hours. $[\alpha]_D^{20°}$ + 72·0° (equilibrium value). Sulphuric acid was removed with barium carbonate and the neutral solution filtered and concentrated under reduced pressure. The residual syrup was exhaustively extracted with acetone, and the extracts concentrated under reduced pressure to a syrup (0·45 g.) which crystallised on exposure to moist air. The crystals were triturated with ethyl acetate and filtered, giving the α-form of the monohydrate of 2 : 4-dimethyl *d*-galactose (0·4 g.), m. p. 105° and mixed m. p. 105° (after recrystallisation from ethyl acetate). The filtrate from crystalline 2 : 4-dimethyl β-methyl-*d*-galactoside was concentrated to a syrup (2·2 g.) which was hydrolysed with N-hydrochloric acid (50 c.c.) during 5 hours. $[\alpha]_D^{19°}$ + 89° (initial value); + 81° (2½ hours); + 76° (3½ hours, constant value). Hydrochloric acid was removed with silver carbonate and the solution filtered and worked up in the usual way to give a syrup (1·8 g.) which crystallised on nucleation with 2 : 4-dimethyl *d*-galactose monohydrate. The syrupy mass was triturated with acetone and filtered. The crystals (0·90 g.) had m. p. and mixed m. p. with an authentic specimen of 2 : 4-dimethyl *d*-galactose monohydrate, 105°. The non-crystalline residue was refluxed with alcoholic aniline giving crystalline 2 : 4-dimethyl *d*-galactose anilide (0·50 g.), m. p. and mixed m. p. 207°. These figures show the presence of 2·34 g. of 2 : 4-dimethyl methyl-*d*-galactoside in this fraction.

Identification of 2 : 4-*Dimethyl* d-*Galactose*.—The sugar (0·50 g.) was dissolved in water (15 c.c.) and periodic acid (1·00 g., excess) added. The rotation of the solution fell from + 84° to + 58° in 40 minutes, and the solution became orange in colour. After 12 hours, the solution was neutralised with barium carbonate and filtered. The filtrate reduced Fehling's solution and contained formaldehyde, recognised by its odour. Evaporation of the filtrate gave a syrup (0·35 g.) which was oxidised with bromine water in the presence of barium carbonate. The solution became non-reducing to Fehling's solution in two hours. Bromine was removed by aeration and the filtered solution evaporated to a syrup and esterified for 8 hours with 2% methyl alcoholic hydrogen chloride. Hydrochloric acid was removed with silver carbonate, the filtered solution evaporated to dryness, and the residue exhaustively extracted with chloroform. Concentration of the extracts gave the dimethyl ester of αα′-dimethoxy β-hydroxy *l*-araboglutaric acid (0·20 g.; $n_D^{19°}$ 1·4495; $[\alpha]_D^{20°}$ + 48° (*c*, 4·0 in methyl alcohol)) which was distilled in a vacuum, b. p. 135°/0·001 mm. (bath temp.), $n_D^{17°}$ 1·4470, $[\alpha]_D^{20°}$ + 50° (*c*, 2·17 in methyl alcohol) (Found : equiv. wt., 123; OMe, 51. Calc. for $C_9H_{16}O_7$: equiv. wt., 118; OMe, 53·3%). The ester with methyl alcoholic ammonia gave the corresponding di-amide in good yield, $[\alpha]_D^{20°}$ + 60° (in water), m. p. 284° (decomp.) after recrystallisation from water–acetone, not depressed on admixture with an authentic specimen supplied by Dr. F. Smith of Birmingham University (Found : N, 13·2. Calc. for $C_7H_{14}O_5N_2$: N, 13·6%).

Fraction IX (1·21 g.), was partially crystalline and was triturated with acetone–ether and filtered. The crystals (0·15 g.) were washed with ether and dried, m. p. 106—110°. These crystals were a mixture of the α- and β-form of 2 : 4-dimethyl methyl-*d*-galactoside, since on hydrolysis with N-hydrochloric acid they gave the monohydrate of 2 : 4-dimethyl *d*-galactose, m. p. and mixed m. p. 105°. The filtrate was concentrated to a syrup (1·06 g.) and hydrolysed with N-hydrochloric acid (50 c.c.). $[\alpha]_D^{19°}$ + 93° (*c*, 2·12, initial value); + 74° (1 hour); + 66° (2 hours, constant value). The solution was neutralised with silver carbonate, filtered and concentrated under reduced pressure to a syrup (0·95 g.). This syrup did not crystallise on nucleation with 2 : 4-dimethyl *d*-galactose monohydrate. It was dissolved in absolute

alcohol (10 c.c.) containing aniline (0·45 c.c.) and heated under reflux for 2 hours. On cooling, 2 : 4-dimethyl *d*-galactose anilide (0·47 g.) separated and was filtered off and washed with alcohol and ether. M. p. and mixed m. p. 207° (decomp.). The filtrate on concentration gave a syrup which crystallised on the addition of a little ether. After standing, the crystals were triturated with alcohol containing ether and filtered off (0·15 g.). The crystals had m. p. 150°, raised to 165° on recrystallisation from alcohol–ether, mixed m. p. with 2-methyl *d*-galactose anilide, 165°. The mother liquors on standing gave a further crop (0·10 g.) of crystals, m. p. and mixed m. p. with 2-methyl *d*-galactose anilide, 165° (see below). The residual syrupy anilides were dark brown, and no crystalline material could be isolated from them. The syrupy anilides were decomposed with hot N-hydrochloric acid (20 c.c.) for 2 hours. Hydrochloric acid was removed as silver chloride and aniline extracted with benzene. The aqueous solution was concentrated to a syrup at 50°/0·12 mm. and the sugars converted to the glycosides (0·20 g.) by refluxing with 2% methyl alcoholic hydrogen chloride (20 c.c.), but, since no crystalline material could be isolated, they were not further investigated.

Fraction X. 2- and 4(?)-Monomethyl *d*-galactose (2·15 g.). This fraction (1·90 g.) was dissolved in N-hydrochloric acid (50 c.c.) and heated on the boiling water-bath for 3 hours, $[\alpha]_D^{21°}$ + 72° (initial value); 80° (1 hour); 76° (3½ hours, constant value). The solution was worked up as described above. Concentration of the neutral aqueous solution gave a syrup (1·75 g.) which rapidly crystallised. Trituration with acetone–methyl alcohol gave crystals (1·1 g.), m. p. 156—180°. Recrystallisation from methyl alcohol and then from glacial acetic acid gave two compounds in approximately equimolecular proportions. A more soluble crystalline fraction was identified as β-2-methyl *d*-galactose, m. p. 147°. $[\alpha]_D^{21°}$ + 49° (*c*, 0·72 in water); + 59° (½ hour); + 65° (1 hour); + 70° (1 hour); + 76·0° (2½ hours); + 80° (6 hours, constant value) (Found : C, 43·4; H, 7·39; OMe, 16·5. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·22; OMe, 16·0%). When heated with alcoholic aniline the sugar gave an anilide, m. p. 165°, not depressed on admixture with a sample of 2-methyl *d*-galactose anilide previously prepared by Dr. F. Smith of Birmingham University (Found : C, 57·6; H, 7·09; N, 5·0; OMe, 9·8. Calc. for $C_{13}H_{19}O_5N$: C, 57·8; H, 7·13; N, 5·2; OMe, 11·5%). On heating with phenylhydrazine in alcohol it gave 2-d-*galactosephenylhydrazone*, m. p. 140—141° (Found : C, 54·8; H, 7·2; N, 9·45. $C_{13}H_{20}O_5N_2$ requires C, 54·8; H, 7·1; N, 9·85%).

The sugar (0·20 g.) on oxidation with bromine in the usual manner gave the syrupy *lactone* of the corresponding acid (0·18 g.), $[\alpha]_D^{20°}$ − 27° (*c*, 1·5 in water) mutarorating very slowly to − 24° (100 hours, value still rising) (Found : equiv. wt., 192; OMe, 16·5. $C_7H_{12}O_6$ requires equiv. wt., 192; OMe, 16·1%).

The lactone on solution in liquid ammonia gave in a syrupy form 2-*methyl galactonamide*, $[\alpha]_D^{22°}$ + 27·0° (*c*, 4·9 in water) (Found : OMe, 14·5. $C_7H_{15}O_6N$ requires OMe, 14·9%). This amide on treatment with sodium hypochlorite under the conditions described by Weerman (*loc. cit.*) gave a negative test showing the presence of a methoxyl group in C_2.

The more insoluble crystalline sugar was β-4(?)-*methyl* d-*galactose*, m. p. 207°, $[\alpha]_D^{20°}$ + 62° (*c*, 1·5 in water), rising to + 92° (in 9 hours) (Found : C, 42·9; H, 7·10; OMe, 16·5. $C_7H_{14}O_6$ requires C, 43·2; H, 7·22; OMe, 16·0%). In cold 1% methyl alcoholic hydrogen chloride, the crystals had $[\alpha]_D^{21°}$ + 126° (*c*, 3·0 — constant value). On heating with alcoholic aniline, the sugar gave 4(?)-*methyl galactose anilide*, m. p. 168° (Found : C, 57·6; H, 7·2; N, 5·36. $C_{13}H_{19}O_5N$ requires C, 57·8; H, 7·13; N, 5·2%). With excess of phenylhydrazine acetate at 70° the sugar gave the *osazone*, m. p. 150° (decomp.) (quoted with reserve since only a small amount of material was available) (Found : OMe, 8·3. $C_{19}H_{24}N_4O_4$ requires OMe, 8·3%.)

The non-crystalline sugars (0·60 g.) on oxidation gave a lactone (0·60 g.), OMe, 17·6%. Equiv. wt. 194. $[\alpha]_D^{20°}$ + 18°, falling to + 9° in 12 hours (*c*, 1·08 in water). Solution in liquid ammonia gave the mixed amides from which 2 : 4-dimethyl *d*-galactonamide (0·10 g.) separated. M. p. and mixed m. p. with an authentic specimen, 164° (after previous sintering at 100°). The residual non-crystalline amide gave a positive Weerman test.

Uronic Acid Fractions.—Fraction XI. A portion (0·56 g.) was hydrolysed with N-hydrochloric acid (25 c.c.) at 90—95° for 12 hours. Owing to opalescence of the solution, change of rotation was not observable. Hydrochloric acid was removed with silver carbonate and hydrogen sulphide bubbled through the filtered solution to remove silver as sulphide and the solution again filtered. Concentration of the filtrate at 40°/12 mm. gave a syrup (0·47 g.), $n_D^{19°}$ 1·4750. OMe, 38·9%. Equiv. wt., 236. $[\alpha]_D^{20°}$ + 54° (in water, *c*, 1·4). The syrup was oxidised with bromine water at 60° for 10 hours. The solution was worked up in the usual way and the residual syrup esterified with methyl alcoholic hydrogen chloride, neutralised with silver carbonate, the methyl alcohol boiled off, and the syrupy residue distilled in a vacuum, b. p. 140°/0·002 mm. (bath temp.), $n_D^{18°}$ 1·4600. The distillate crystallised to a solid mass of methyl 2 : 3 : 4-trimethyl *d*-saccharolactone, m. p. and mixed m. p. 110° (after recrystallisation from ether). $[\alpha]_D^{20°}$ + 100° (*c*, 0·6 in alcohol).

Fractions XII and XIII (1·10 g.) were combined and hydrolysed with N-hydrochloric acid (30 c.c.) at 90—95° during 5 hours. $[\alpha]_D^{20°}$ changed from + 72° to + 30° (constant value). The solution was worked up as for Fraction XI (above), giving a syrup (0·78 g.), $n_D^{18°}$ 1·4880, $[\alpha]_D^{20°}$ + 36° (in water, *c*, 1·7) (Found : equiv. wt., 224; OMe, 32·6. Calc. for 2 : 3-dimethyl *d*-glycuronic acid, $C_8H_{14}O_7$: equiv. wt., 224; OMe, 27·7%).

The sugar acid (0·70 g.) was oxidised with bromine water and worked up as above and the dimethyl saccharic acid esterified and distilled in a vacuum, b. p. 140—170°/0·002 mm., $n_D^{18°}$ 1·4700. The distillate crystallised on standing and by trituration with warm ether the crystals were separated into ether-soluble 2 : 3 : 4-trimethyl methyl-*d*-saccharolactone, m. p. and mixed m. p. 110°, and ether-insoluble 2 : 3-dimethyl methyl-*d*-saccharolactone, m. p. and mixed m. p. with an authentic specimen 101°, depressed to 81° on admixture with 2 : 3 : 4-trimethyl methylsaccharolactone (Found : C, 46·2; H, 6·1; OMe, 38·3. Calc. for $C_9H_{14}O_7$: C, 46·2; H, 6·0; OMe, 39·7%).

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