191. *The Constitution of Arabic Acid. Part V. Methylated Arabic Acid.*

By F. Smith.

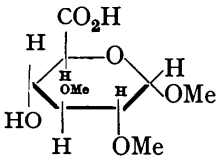
Methylation of arabic acid or gum arabic with methyl sulphate affords *methylated arabic acid*; treatment of the latter with Purdie's reagents effects esterification and completes the methylation to give the *methyl* ester of methylated arabic acid. When this ester is boiled with methyl-alcoholic hydrogen chloride, simultaneous hydrolysis and glycoside formation take place with the formation of 2 : 3 : 4-trimethyl methyl-*l*-rhamnopyranoside, 2 : 5-dimethyl and 2 : 3 : 5-trimethyl methyl-*l*-arabofuranoside, 2 : 3 : 4 : 6-tetramethyl methyl-*d*-galactopyranoside, 2 : 4-dimethyl methyl-*d*-galactoside, the methyl ester of 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside, and the *methyl* ester of 2 : 3-*dimethyl methyl*-d-*glucuronoside*. The identification of these hydrolysis products demonstrates the branched-chain structure of arabic acid and also shows that those labile sugar residues, namely, *l*-arabinose, *l*-rhamnose, and 3-galactopyranosido-*l*-arabinose, which are liberated during the autohydrolysis of arabic acid are joined to the nucleus of degraded arabic acid in the form of *l*-arabofuranose, *l*-rhamnopyranose, and 3-galactopyranosido-*l*-arabofuranose. In addition to the 1 : 3- and 1 : 6-linkages, shown by previous investigations and by the present work to exist in arabic acid, the 1 : 4-linkage is now proved to be present by the isolation of the methyl ester of 2 : 3-dimethyl methylglucuronoside as one of the cleavage products of methylated arabic acid. The type of structure which may be present in arabic acid is discussed.

In Part I (Smith, J., 1939, 744) the mixture of reducing sugars liberated by the autohydrolysis of arabic acid was shown to consist of *l*-arabinose, *l*-rhamnose, and a disaccharide, 3-galactosido-*l*-arabinose. In view of the relative ease of removal of these sugar residues from the stable nucleus of degraded arabic acid, during autohydrolysis, it was tentatively suggested that the arabinose and rhamnose residues and the arabinose moiety of the 3-galactopyranosido-*l*-arabinose exist in arabic acid in the furanose form. In order to determine the precise form which these labile sugar residues assume in the polysaccharide and the mode of attachment by which they are united to the nucleus of degraded arabic acid, the methyl derivative of arabic acid has been subjected to examination.

Methylated arabic acid was prepared by treating either arabic acid or gum arabic with methyl sulphate and sodium hydroxide, followed by esterification and complete methylation with Purdie's reagents. When the methyl ester of methylated arabic acid, prepared in this way, was boiled with methyl-alcoholic hydrogen chloride, simultaneous hydrolysis and glycoside formation took place and there was produced a mixture of the following seven glycosides: 2 : 3 : 4 : 6-tetramethyl methyl-*d*-galactoside, 2 : 4-dimethyl methyl-*d*-galactoside, 2 : 3 : 5-trimethyl methyl-*l*-arabinoside, 2 : 3 : 4-trimethyl methyl-*l*-rhamnoside, 2 : 5-dimethyl methyl-*l*-arabinoside, and the methyl esters of 2 : 3-dimethyl and 2 : 3 : 4-trimethyl methyl-*d*-glucuronoside. This mixture was treated with barium hydroxide, whereby the ester components were converted into a mixture of barium salts (A), from which the glycosides (B) were separated by extraction with ether.

The structure of the *dimethyl methylglucuronoside* (I) obtained by treating the barium salt (A) with sulphuric acid was ascertained in the following way. On boiling the barium salt with acid methyl alcohol it gave the corresponding *methyl* ester (II), which was characterised as the *phenylhydrazide*. The presence of one free hydroxyl group in (II) was established by the fact that on treatment with *p*-nitrobenzoyl chloride it yielded a *mono-p-nitrobenzoate*. Inasmuch as it has been shown that the glucuronic acid residues of degraded arabic acid possess pyranose structures, it follows that the corresponding uronic acid residues of arabic acid which furnish the dimethyl methylglucuronoside (I) and the ester (II) must also have pyranose structures; the possibility of either of the two methyl groups occupying position 5 is therefore ruled out and consequently the two methyl groups in (I) and (II) must be situated at the positions 2 : 3, 2 : 4, or 3 : 4. This view was confirmed by the observation that methylation of (II) with Purdie's reagents gave the methyl ester of 2 : 3 : 4-trimethyl methylglucuronoside (III), which was identified by its conversion into

the crystalline amide (IV) of 2 : 3 : 4-trimethyl α-methylglucuronoside (Smith, Part II, J., 1939, 1724).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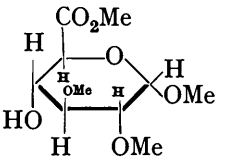
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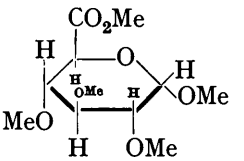
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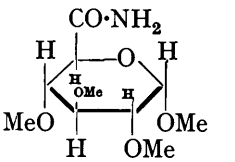
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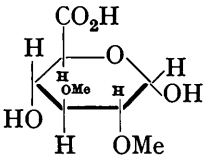

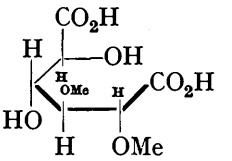
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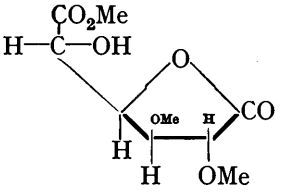
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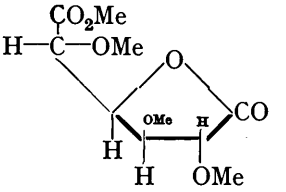
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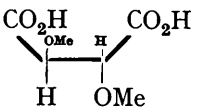
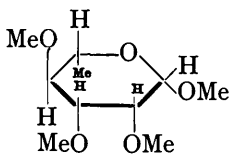

(IX.)

When (II) was subjected to hydrolysis with dilute sulphuric acid, the methyl group at C_1 and the ester methyl group at C_6 were removed with the formation of the dimethyl glucuronic acid (V), which, on oxidation with bromine, furnished the dimethyl saccharic acid (VI); the latter was not isolated but it was transformed, by esterification and subsequent distillation, into the crystalline *dimethyl saccharolactone methyl ester* (VII). This lactone methyl ester was also obtained from (II) by oxidation with nitric acid, followed by esterification and subsequent distillation. The dimethyl saccharolactone methyl ester (VII) showed relatively slow hydrolysis in aqueous solution and hence it seemed probable that the lactone ring was of the γ-type. This view was confirmed when it was shown that methylation of (VII) with silver oxide and methyl iodide afforded crystalline 2 : 3 : 5-*trimethyl γ-saccharolactone methyl ester* (VIII). The constitution of the latter is apparent from its preparation by the oxidation of 2 : 3 : 5-trimethyl methylglucofuranoside with nitric acid, followed by esterification and subsequent distillation (unpublished results). The presence of the 1 : 4-lactone ring in (VII) and (VIII) proves that the original dimethyl methylglucuronoside (II) must carry a free hydroxyl group at C_4 and that the two methyl groups in (I) and (II) must occupy the positions 2 and 3. The correctness of this conclusion was borne out by the observation that oxidation of both the methyl ester of the dimethyl methylglucuronoside (II) and the corresponding dimethyl γ-saccharolactone methyl ester (VII) with nitric acid gave *l*(+)-threodimethoxysuccinic acid (*d*-dimethoxysuccinic acid) (IX), identified as the crystalline diamide. The formulations assigned to (I) and (II) were further confirmed by the fact that 2 : 3-dimethyl γ-saccharolactone methyl ester prepared from 2 : 3-dimethyl glucose proved to be identical in every respect with the dimethyl saccharolactone methyl ester prepared from (II). It is of interest to note that 2 : 3-dimethyl glucuronic acid has been identified as one of the cleavage fragments of methylated degraded damson gum (Hirst and Jones, J., 1939, 1482).

The methyl ester of the trimethyl methylglucuronoside was characterised as the 2 : 3 : 4-trimethyl derivative by the fact that (*a*) on treatment with methyl-alcoholic ammonia it afforded the crystalline amide (IV) of 2 : 3 : 4-trimethyl α-methylglucuronoside and (*b*) when subjected to hydrolysis with dilute sulphuric acid it furnished 2 : 3 : 4-trimethyl glucuronic acid, which undergoes smooth oxidation with bromine to the corresponding 2 : 3 : 4-trimethyl saccharic acid, identified as the known crystalline 2 : 3 : 4-trimethyl δ-saccharolactone methyl ester (see Part II).

The mixture of methylated glycosides (B) was separated into a light-petroleum-soluble fraction (C) containing 2 : 3 : 5-trimethyl methylarabinoside, 2 : 3 : 4-trimethyl methylrhamnoside, 2 : 3 : 4 : 6-tetramethyl methylgalactoside, and 2 : 5-dimethyl methylarabinoside, and a light-petroleum-insoluble fraction (R) consisting of 2 : 4-dimethyl methylgalactoside. Complete resolution of fraction (C) into its constituents could not be effected by fractional distillation for the reason that two constant-boiling mixtures were formed, one (H) by the trimethyl methylarabinoside and the trimethyl methylrhamnoside and the other (K) by the dimethyl methylarabinoside and the tetramethyl methylgalactoside.

An attempt was made to utilise the fact that furanosides are more easily hydrolysed than pyranosides and accordingly the constant-boiling mixture (H) consisting of the furanoside (X) and the pyranoside (XI) was subjected to hydrolysis with 0·1N-sulphuric acid; since, however, the trimethyl methylrhamnopyranoside was hydrolysed under these conditions as well as the trimethyl methylarabofuranoside, their separation could not be effected in this manner. The constant-boiling mixture (H) consisting of equimolecular proportions of (X) and (XI) was completely hydrolysed by heating with dilute sulphuric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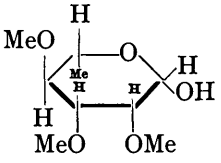
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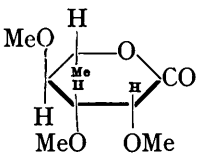
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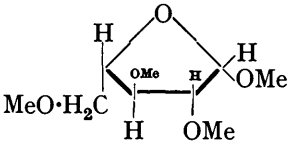

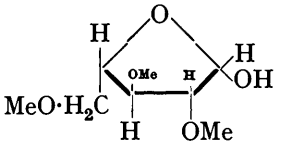
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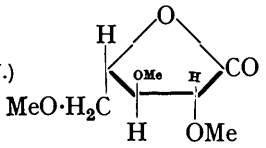
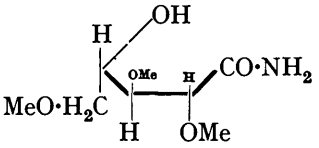
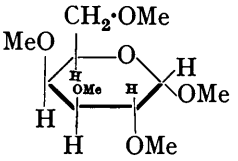



(XVI.

acid and the presence of 2 : 3 : 4-trimethyl rhamnose (XII) in the resulting mixture of sugars was ascertained by preparing from it crystalline 2 : 3 : 4-trimethyl rhamnose anilide. Confirmation of the structure of the rhamnose derivative was forthcoming from an examination of the mixture of the two lactones (XIV) and (XV) obtained by bromine oxidation of the mixture of the reducing methylated sugars (XIII) and (XII) respectively; treatment of this lactone mixture with phenylhydrazine furnished the crystalline phenylhydrazide of 2 : 3 : 4-trimethyl rhamnonic acid. The arabinose component was identified by treating the mixture of lactones with methyl-alcoholic ammonia, whereby there was produced the characteristic crystalline amide (XVI) of 2 : 3 : 5-trimethyl arabonic acid (Humphreys, Pryde, and Waters, J., 1931, 1298).

The second constant-boiling mixture encountered (K) appeared to consist of equimolecular proportions of the tetramethyl methylgalactoside (XVII) and the dimethyl methylarabinoside (XVIII) (see Part I). In this case the difference in the stability of the two glycosides towards dilute mineral acid could be employed in order to effect a separation. Thus, when the mixture of (XVII) and (XVIII) was heated with 0·1N-sulphuric acid, (XVIII) was preferentially hydrolysed and fractional distillation of the product gave a lower-boiling first fraction of the unchanged tetramethyl methylgalactoside (XVII) and a second fraction which was a constant-boiling mixture of the dimethyl arabinose (XIX) and tetramethyl galactose (XX). The tetramethyl methylgalactoside (XVII) which comprised the whole of the fraction of lower boiling point was characterised by the fact that it gave, on hydrolysis, crystalline 2 : 3 : 4 : 6-tetramethyl galactose (XX) and this in turn furnished the known crystalline anilide of 2 : 3 : 4 : 6-tetramethyl galactose. The

presence of 2 : 3 : 4 : 6-tetramethyl galactose in the constant-boiling mixture of (XIX) and (XX) was shown by the fact that on treatment of this mixture with ethyl-alcoholic aniline there was obtained crystalline 2 : 3 : 4 : 6-tetramethyl galactose anilide. Confirmation of the presence of (XX) in the mixture and proof that the latter also contained 2 : 5-dimethyl arabinose were forthcoming from an examination of the corresponding mixture of the lactones (XXI) and (XXII) derived from it by the agency of bromine. When this lactone mixture was treated with an ethereal solution of phenylhydrazine at room temperature, there separated the crystalline phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl galactonic acid and from the mother-liquors there was isolated the crystalline phenylhydrazide of 2 : 5-dimethyl arabonic acid. Furthermore, when the mixture of (XXI) and (XXII) was allowed to react with methyl-alcoholic ammonia, it afforded the crystalline amide (XXIII) of 2 : 5-dimethyl arabonic acid, identical with a specimen previously prepared from the arabinose moiety of heptamethyl 3-galactosido-*l*-arabofuranose (Part I).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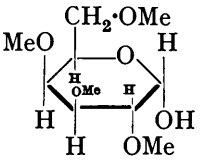
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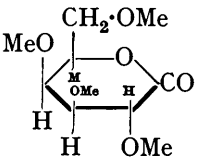
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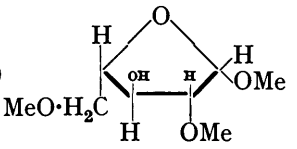

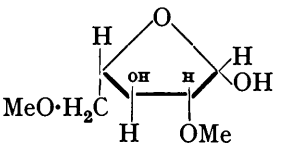
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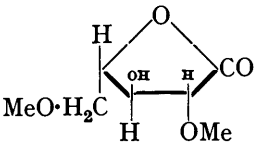
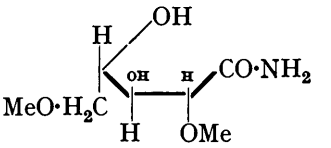
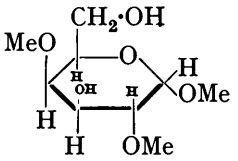



(XXIII.)

The dimethyl methylgalactoside which constituted the fraction (R) insoluble in light petroleum (see above) crystallised as a mixture of the α- and the β-form, which were separated and shown to be identical with the corresponding forms of 2 : 4-dimethyl methylgalactoside previously obtained from methylated degraded arabic acid (Part II). Furthermore, when specimens of the two forms of the dimethyl methylgalactoside (XXIV) were subjected to hydrolysis, they gave the same 2 : 4-dimethyl galactose (XXV) (isolated as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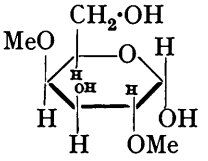
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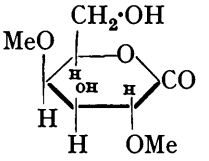
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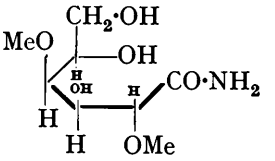

(XXVII.)

the crystalline monohydrate), from which there was prepared by means of bromine oxidation the corresponding crystalline 2 : 4-dimethyl δ-galactonolactone (XXVI). The latter was identified by melting point and comparison with an authentic specimen (see Part II). Moreover, on treatment with ammonia in methyl alcohol, (XXVI) furnished the known amide (XXVII) of 2 : 4-dimethyl galactonic acid and with phenylhydrazine it was smoothly transformed into the corresponding crystalline phenylhydrazide of 2 : 4-dimethyl galactonic acid.

A review of the investigations described in this communication and those recorded in Parts I—IV emphasises the complex nature of arabic acid as compared with the more commonly occurring polysaccharides of plant origin. Starch, for example, is built up only

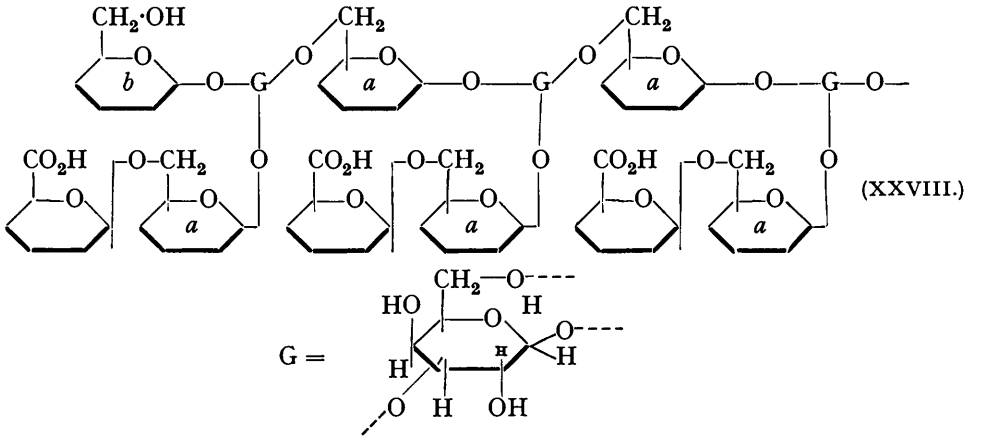
of glucose units and the simplest interpretation of the structure of its repeating unit is that it is a terminated chain of glucopyranose residues joined by one type of link, the 1 : 4-link (see Hirst and Young, J., 1939, 1471). In arabic acid, however, not only do different monosaccharide residues constitute the fundamental or repeating unit, but these residues are mutually joined by no less than three different types of linkage, namely the 1 : 6-, the 1 : 3-, and the 1 : 4-linkages.

The existence of the 1 : 6-type of linkage in arabic acid has been established (*a*) by the isolation of 6-β-glucuronosidogalactose from arabic acid (Challinor, Haworth, and Hirst, J., 1931, 258), (*b*) by the formation of hexamethyl 6-β-glucuronosidogalactose by graded hydrolysis of methylated arabic acid (Jackson and Smith, Part III, this vol., p. 74), and (*c*) by the isolation of 2 : 3 : 4-trimethyl galactose as one of the cleavage products of methylated degraded arabic acid (Part II).

Proof of the presence of the 1 : 3-link is based upon the following experimental observations: (*a*) autohydrolysis of arabic acid produces degraded arabic acid and a mixture of three reducing sugars, one of which has been shown to be 3-galactosido-*l*-arabinose (Part I), (*b*) prolonged autohydrolysis of the degraded arabic acid affords the disaccharide, 3-galactosidogalactose (Jackson and Smith, Part IV, this vol., p. 79), and (*c*) by the identification of 2 : 5-dimethyl *l*-arabinose as one of the hydrolysis products of methylated arabic acid (this paper). In addition, the presence of 1 : 6- and also of 1 : 3-types of linkage has been established by the identification of 2 : 4-dimethyl galactose as one of the hydrolytic products of both methylated degraded arabic acid (Part II) and methylated arabic acid (this paper).

Since the glucuronic acid residues of degraded arabic acid have been shown to have pyranose structures, so the corresponding glucuronic acid units of the original arabic acid must also possess pyranose structures; it follows, therefore, that the isolation of 2 : 3-dimethyl glucuronic acid described above can only be interpreted by the presence in arabic acid of the third type of linkage, namely, the 1 : 4-link.

In order to explain the constitutional significance of the identification of the 2 : 3 : 5-trimethyl and 2 : 5-dimethyl methyl-*l*-arabinosides, the 2 : 3 : 4-trimethyl methyl-*l*-rhamnoside, 2 : 3 : 4 : 6-tetramethyl and 2 : 4-dimethyl methylgalactoside, and the methyl esters of 2 : 3 : 4-trimethyl and 2 : 3-dimethyl methylglucuronoside, it is helpful to refer to the tentative formulation (XXVIII) for the structure of the repeating unit of degraded arabic acid. This structure was advanced in order to explain the experimental results previously obtained (Part IV). Such an expression shows the existence of the 1 : 3- and the 1 : 6-type of linkage; it explains the observation (Part II) that methylated degraded arabic acid gives on hydrolysis 2 : 3 : 4 : 6-tetramethyl galactose (1 part), 2 : 3 : 4-trimethyl glucuronic acid (3 parts), 2 : 4-dimethyl galactose (3 parts), and 2 : 3 : 4-trimethyl galactose

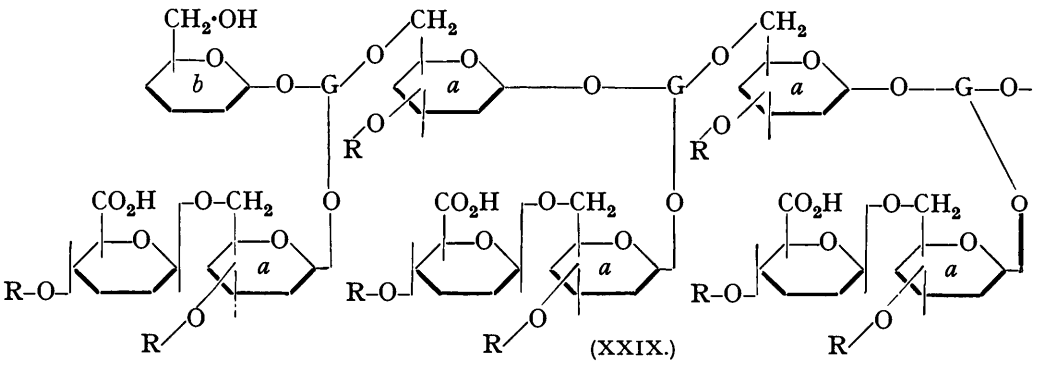


(XXVIII.)

(5 parts); and the reason for the formation of 3-galactosidogalactose from degraded arabic acid (Part IV) and of hexamethyl 6-β-glucuronosidogalactose (Part III) from methylated degraded arabic acid is also forthcoming. The galactopyranose unit G is known to be united

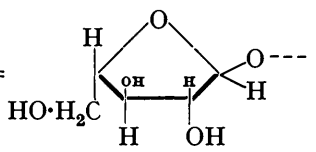
to other residues by a 1 : 6- and a 1 : 3-linkage because it gives rise to 2 : 4-dimethyl galactose; it is represented in this manner, however, because it is not yet clear whether it is joined to the other galactopyranose units in the main chain by a 1 : 3-linkage and to the side chain residues of aldobionic acid by a 1 : 6-linkage, or whether the reverse is the case; furthermore it should be pointed out that it is not yet certain that all the side chains are attached by the same type of link to the main galactose chain.

Another feature worthy of note, revealed by the work on degraded arabic acid and confirmed by the present communication, is the branched-chain structure of arabic acid to which attention has previously been drawn (Smith, *Chem. and Ind.*, 1939, **58**, 203). The expression (XXVIII) shows four terminal groups, one of galactose and three of glucuronic acid. Now methylated degraded arabic acid furnishes five molecular proportions of 2 : 3 : 4-trimethyl galactose, but so far neither the latter nor any other trimethyl derivative of galactose has been detected among the cleavage products of methylated arabic acid. The provisional conclusion is therefore reached that to each of the five galactose residues designated *a* in (XXVIII), which give rise to the 2 : 3 : 4-trimethyl galactose, there must be attached in arabic acid itself other residues R as shown in (XXIX), and since each of the

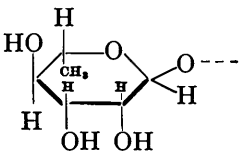


(XXIX.)

(XXX.) R =

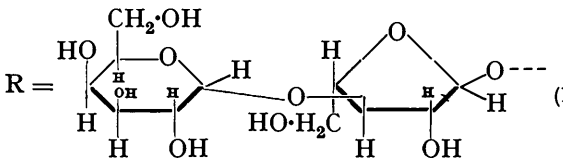


R =



(XXXI.)

R =



(XXXII.)

residues R furnishes an end group, the number of terminal groups in the repeating unit of arabic acid is nine. As a result of the attachment of the terminal residues R to position 3 of each of the galactose units *a*, then, the units *a* as well as the galactose units represented by G in formula (XXIX) will furnish 2 : 4-dimethyl galactose.

It has been shown that in degraded arabic acid all the uronic acid units constitute end groups, but this is not the case with the original arabic acid. In the latter the uronic acid groups must occupy intermediate positions in the side chains, because almost the whole of the glucuronic acid is present as the 2 : 3-dimethyl derivative. This fact is expressed in (XXIX) by the extension of the acid side chains through the union of a residue R with position 4 of the glucuronic acid residue. With these requirements satisfied, there results the tentative formulation (XXIX) for the type of structure which may constitute the repeating unit of arabic acid.

The identification of a small amount of the acid component of methylated arabic acid

as 2 : 3 : 4-trimethyl glucuronic acid may indicate that some degradation has taken place during the preparation of methylated arabic acid with consequent scission of a residue R from the uronic acid residue, or it may mean that some glucuronic acid residues constitute terminal groups in the polysaccharide complex; this observation requires further investigation.

The separation and identification of the constituents of the mixture of glycosides derived from methylated arabic acid is not an easy problem and it is realised that there may be other substances present in the mixture which have escaped detection. A further examination of the cleavage products from a larger amount of methylated arabic acid is therefore being carried out.

The residues R are obviously composed of those sugar residues (*l*-arabinose, *l*-rhamnose, and 3-galactosidoarabinose) which are eliminated from the stable nucleus of arabic acid during autohydrolysis. It is not claimed that the residues R represent single monosaccharide units; indeed the isolation of the disaccharide 3-galactosidoarabinose proves that, in part at least, R represents a side chain of two monosaccharide units. Nevertheless an estimate may be made of the nature of the terminating units of the side chains R. Thus the isolation of the whole of the rhamnose and part of the arabinose as 2 : 3 : 4-trimethyl rhamnopyranose and 2 : 3 : 5-trimethyl arabofuranose respectively from methylated arabic acid shows that some of the side chains, R, are terminated by rhamnopyranose units and some by arabofuranose residues. Moreover, galactopyranose must be present in the repeating unit of the polysaccharide as end groups terminating side chains, because 2 : 3 : 4 : 6-tetramethyl galactopyranose was recognised as a cleavage product of methylated arabic acid. Those side chains which afford the disaccharide, 3-*d*-galactosido-*l*-arabinose (obtained during the autohydrolysis of arabic acid), are terminated in all probability by the galactose moiety and would therefore give rise to the 2 : 3 : 4 : 6-tetramethyl galactose either wholly or in part. In this connection it should be borne in mind that a galactopyranose residue (*b* in XXIX) constitutes an end in the repeating unit of degraded arabic acid and this end group is not linked to an arabinose unit; it is also conceivable that in arabic acid a side chain residue R may be attached to this galactose residue *b*.

A portion of the arabinose constituent of arabic acid is isolated from methylated arabic acid as 2 : 5-dimethyl arabofuranose and this must therefore represent arabinose units which are interposed between the terminal groups of the side chains and the nucleus of degraded arabic acid. The isolation of the 3-galactosido-*l*-arabinose fragment from arabic acid lends support to this view, and the identification of the 2 : 5-dimethyl arabinose strongly suggests that in the polysaccharide the disaccharide is present in the form of 3-galactosido-*l*-arabofuranose. It may well be that arabofuranose units are also interposed between the nucleus (degraded arabic acid) and the terminal groups, rhamnopyranose and arabofuranose, and the resulting side chains would conform in type to that represented by 3-galactosidoarabinose. At the present time, however, there is no evidence available to support such an assumption and the simplest expression of the known facts is that the residues represented by R in (XXIX) consist of *l*-arabofuranose (XXX), *l*-rhamnopyranose (XXXI), and 3-galactosidoarabofuranose (XXXII).

Experimental.

Methylated Arabic Acid.—A solution of gum arabic or arabic acid (20 g.) in sodium hydroxide (100 c.c. of a 30% solution) was treated with methyl sulphate (250 c.c.) and sodium hydroxide (600 c.c. of a 30% solution) at room temperature, the reagents being added gradually during 4 hours with vigorous stirring. The process of methylation, which was accompanied by much frothing, was completed by continuing the stirring for a further period of 9 hours. The mixture was then cooled in ice and almost neutralised with 15N-sulphuric acid; the alkaline solution was filtered through linen to remove the sodium sulphate which had crystallised and evaporated to a suitable volume (100—150 c.c.). The process of methylation was then repeated, the same quantities of reagents and the same conditions being used. After the second methylation and sometimes after the first, concentration of the alkaline solution after removal of sodium sulphate resulted in the separation of the sodium salt of the partially methylated gum in pale yellow, plastic nodules; the latter could then be separted mechanically and remethylated. This

crude sodium salt of methylated arabic acid was readily soluble in water and in hot methyl alcohol; it was insoluble in ethyl alcohol, acetone, ether, and chloroform but readily dissolved in aqueous acetone. For the third methylation, therefore, the crude sodium salt was dissolved in aqueous acetone (60 c.c. of water and 40 c.c. of acetone) and treated with methyl sulphate (250 c.c.) and sodium hydroxide (750 c.c. of a 30% solution) at 35°; the reagents were added in tenth quantities at intervals of 15 minutes, and in order to keep the sodium salt of the partially methylated arabic acid in solution, acetone was added from time to time. To prevent the elimination of any labile sugar residues, care was taken that during the methylation the solution was always alkaline. The methylation was completed by heating the solution for 15 minutes at 65°, whereby the excess of the acetone was expelled and the sodium salt of methylated arabic acid separated on the surface of the methylation mixture as insoluble, pale yellow nodules. The latter were filtered off while the solution was still hot, since the sodium salt of methylated arabic acid was found to be less soluble in hot than in cold water. After three more methylations at 35° (six methylations in all) a portion of the crude sodium salt of methylated arabic acid in water was treated with a slight excess of 5N-sulphuric acid; in this way the methylated arabic acid was precipitated as a white powder, which was extracted with chloroform; the chloroform extract was washed twice with a saturated solution of sodium sulphate, dried over anhydrous sodium sulphate, filtered, and then concentrated under reduced pressure. When the concentrated chloroform solution was poured into excess of light petroleum with stirring, the methylated arabic acid was obtained as a white amorphous powder, which, when dried by heating at 60° in a vacuum, was examined in respect of its methoxyl content. Methylation of the remainder of the crude sodium salt was then repeated, and a portion purified after each methylation, as described above, in order to determine when complete methylation had been reached. The results show that even after six methylations the product was completely methylated [Found: OMe, 38·9 (after 5 methylations); 38·2 (after 7); 38·7 (after 8); 39·5 (after 10); 39·2 (after 13); 39·1 (after 15); 39·2% (after 20)]. Usually the gum was methylated ten times and after one precipitation from chloroform solution with light petroleum the yield of methylated arabic acid was *ca.* 12 g. Methylated arabic acid was soluble in water, methyl and ethyl alcohols, acetone, and chloroform but insoluble in ether and light petroleum; its aqueous solution reacted acid to litmus and Congo-paper but did not reduce Fehling's solution even on prolonged boiling. It was precipitated as a syrup from aqueous solution by boiling, especially if a little acetic acid or mineral acid or inorganic salt such as sodium sulphate was added. The methylated arabic acid prior to purification had $[\alpha]_D^{18°}$ — 50° in chloroform (*c*, 1·1), equiv. wt. 1300 (by direct tiration with sodium hydroxide). Fractional precipitation of the methylated arabic acid (50 g.) from a chloroform solution was effected by means of light petroleum. A solution of each fraction precipitated by this method as a syrup, in acetone, was poured with stirring into light petroleum; the white amorphous powder was filtered off, washed with light petroleum, and dried in a vacuum at 60°. The methylated arabic acid appeared to be essentially homogeneous and had $[\alpha]_D^{18°}$ — 47° in chloroform (*c*, 1·0); $\eta_{sp.}^{20°}$ 0·25 in *m*-cresol (*c*, 1·15); equiv. wt. *ca.* 1350; *M*, 90,000 (from osmotic pressure measurements carried out by Dr. S. R. Carter and Dr. Chambers in this Department) (Found: C, 51·4; H, 7·9; OMe, 39·0%).

The methyl ester of methylated arabic acid was prepared by treating a methyl-alcoholic solution of methylated arabic acid with a slight excess of ethereal diazomethane; after keeping for 5 minutes at room temperature, the excess of the solvent was removed under diminished pressure, and the residue subjected to two treatments with Purdie's reagents. The methyl ester of methylated arabic acid prepared in this way reacted neutral to litmus; it was less soluble in water and it seemed to be more soluble in organic solvents than the original methylated acid; it showed $[\alpha]_D^{24°}$ — 48° in chloroform (*c*, 1·5) (Found: C, 52·4; H, 7·8; OMe, 41·9%).

Hydrolysis of Methylated Arabic Acid.—Hydrolysis with dilute mineral acid was found to be impracticable because the methylated arabic acid was precipitated from solution on heating and even when glacial acetic acid was added as a solvent, the hydrolysis which took place was accompanied by decomposition, carbon dioxide being slowly evolved, and among the products of hydrolysis reductinic acid was detected (cf. Reichstein and Oppenauer, *Helv. Chim. Acta*, 1934, **17**, 996, 1003). The evolution of carbon dioxide and the formation of reductinic acid may have been due to the decomposition of the glucuronic acid residues and this was supported by the observation that the partly degraded methylated arabic acid recovered after hydrolysis with dilute mineral and acetic acid had a much higher equivalent weight than the original methylated arabic acid. After two crystallisations from ethyl alcohol the reductinic acid had m. p. 209°, equiv. 113. This unsaturated substance reacted acid to litmus and Congo-paper,

reduced Fehling's solution actively, and immediately decolourised aqueous solutions of iodine, bromine, and potassium permanganate. The substance was optically inactive (Found: C, 52·5; H, 5·2. Calc. for $C_5H_8O_3$: C, 52·6; H, 5·2%).

Hydrolysis of the Methyl Ester of Methylated Arabic Acid.—When a solution of the methyl ester of methylated arabic acid (31·1 g.) in 4% methyl-alcoholic hydrogen chloride (800 c.c.) was boiled under reflux, simultaneous hydrolysis and glycoside formation took place; the following rotational changes were observed: $[\alpha]_D$ − 33° (initial value); + 11° (3 hours); + 15° (4 hours); + 17° (5 hours); + 18° (6 hours); + 19° (7 hours); + 19·5° (8 hours); + 20° (9½ hours). The solution ($[\alpha]_D$ + 20°) was neutralised with silver carbonate, filtered, and evaporated to dryness under slightly reduced pressure, giving a fairly mobile, neutral, pale yellow liquid which did not reduce Fehling's solution.

The product thus obtained was treated with barium hydroxide (250 c.c., 0·3N) for 1½ hours at 60°; the solution was then neutralised by a stream of carbon dioxide, filtered, and evaporated to dryness and in this way there was obtained a pale yellow syrup consisting of the barium salts of methylated glucuronic acids and a mixture of methylated glycosides. This syrup was exhaustively extracted with dry ether and there remained the ether-insoluble, pale yellow barium salt (A) (yield, 7·7 g.). Concentration of the ethereal extract gave a mixture of methylated glycosides (B) (26 g.), which was then exhaustively extracted with boiling light petroleum to give a fraction (C) (11·5 g.); there remained a petroleum-ether-insoluble residue (R) (14·2 g.).

Examination of the Barium Salt (A) and the Identification of 2 : 3-*Dimethyl Methylglucuronoside* (I).—The barium salt (7·7 g.) was dissolved in water and treated with a slight excess of dilute sulphuric acid; the solution was then neutralised with lead carbonate and filtered. The filtrate was treated with hydrogen sulphide, filtered, and evaporated to dryness under reduced pressure, giving 2 : 3-*dimethyl methylglucuronoside*. In order to determine whether lactone formation would take place, a small portion of this free acid ($[\alpha]_D^{18°}$ + 68° in water, *c* 1·0) was distilled, giving a viscous liquid, b. p. (bath temp.) 186°/0·03 mm., $[\alpha]_D^{18°}$ + 65° (constant value) in water (*c*, 1·0). The distillate did not behave as a lactone; it reacted acid to litmus and Congo-paper and it could be titrated directly with sodium hydroxide like the original acid (Found: OMe, 39·7. $C_9H_{16}O_7$ requires OMe, 39·4%).

Esterification of the 2 : 3-dimethyl methylglucuronoside was effected by boiling it with 2·5% methyl-alcoholic hydrogen chloride (200 c.c.) for 8 hours. The solution was cooled, neutralised with silver carbonate, filtered, and evaporated to dryness, giving mainly the methyl ester of 2 : 3-dimethyl methylglucuronoside (5·7 g.), a small portion of which distilled, b. p. (bath temp.) 145—150°/0·02 mm., $n_D^{18°}$ 1·4600; $[\alpha]_D^{16°}$ + 70° in water (*c*, 0·9) (Found: OMe, 49·8; equiv., 258. Calc. for $C_{10}H_{18}O_7$: OMe, 49·6%; equiv. 250. Calc. for $C_{11}H_{20}O_7$: OMe, 58·7%; equiv., 264).

Fractional distillation of the main bulk of the methyl ester gave: Fraction I (0·9 g.), b. p. (bath temp.) 120°/0·04 mm., $n_D^{20°}$ 1·4500, $[\alpha]_D^{20°}$ + 53° in water (Found: equiv., 264; OMe, 53·8%). The presence of the methyl ester of 2 : 3 : 4-trimethyl methylglucuronoside in this fraction was proved by the fact that (*a*) on treatment with methyl-alcoholic ammonia it gave a small amount of the amide of 2 : 3 : 4-trimethyl α-methylglucuronoside, m. p. and mixed m. p. 183°, $[\alpha]_D^{20°}$ + 137·5° in water (*c*, 0·9) (after recrystallisation from ethyl alcohol–ether–light petroleum), and (*b*) when subjected successively to hydrolysis, oxidation with bromine, esterification, and subsequent distillation as previously described (Smith, J., 1939, 1724) it yielded 2 : 3 : 4-trimethyl δ-saccharolactone methyl ester, m. p. and mixed m. p. 107° (after crystallisation from ether). Fraction II (4·3 g.), the *methyl* ester of 2 : 3-dimethyl methylglucuronoside, b. p. (bath temp.) 145°/0·04 mm., $n_D^{18°}$ 1·4620, $[\alpha]_D^{18°}$ + 76° in water (*c*, 0·7) (Found: OMe, 49·5; equiv., 254. $C_{10}H_{18}O_7$ requires OMe, 49·6%; equiv., 250).

Methylation of the Methyl Ester of 2 : 3-*Dimethyl Methylglucuronoside.*—The methyl ester of 2 : 3-dimethyl methylglucuronoside (0·3 g.) was completely methylated by one treatment with Purdie's reagents. The product, isolated by means of acetone, was boiled with 3% methyl-alcoholic hydrogen chloride (200 c.c.) for 8 hours; the solution was cooled, neutralised with silver carbonate, filtered, and evaporated to dryness, giving a syrup which distilled, b. p. (bath temp.) 125°/0·03 mm., $n_D^{21°}$ 1·4463, $[\alpha]_D^{18°}$ + 85° in water (*c*, 1·7) (Found: OMe, 59·0; equiv., 262. Calc. for $C_{11}H_{20}O_7$: OMe, 58·7%; equiv., 264). When this ester was treated with methyl-alcoholic ammonia, there was obtained the amide of 2 : 3 : 4-trimethyl α-methylglucuronoside, m. p. and mixed m. p. 183°, $[\alpha]_D^{18°}$ + 139° in water (*c*, 4·0) (after crystallisation from ethyl alcohol–ether).

Derivatives of the Methyl Ester of 2 : 3-*Dimethyl Methylglucuronoside.*—(a) *With phenyl-*

hydrazine. The methyl ester (0·1 g.) was heated for 5 hours at 110° with phenylhydrazine (1 mol.); on cooling, crystals of the *phenylhydrazide* of 2 : 3-dimethyl methylglucuronoside were obtained, m. p. 225—227° (after recrystallisation from acetone–ether–light petroleum) (Found : OMe, 27·7; N, 8·7. $C_{15}H_{22}O_6N_2$ requires OMe, 28·6; N, 8·6%). (b) *With* p-*nitrobenzoyl chloride*. A solution of the methyl ester (0·1 g.) in pyridine (0·3 c.c.) was treated with *p*-nitrobenzoyl chloride (1 mol.) for 4 days at room temperature. The crystalline mixture was then triturated with a saturated solution of sodium bicarbonate and the white precipitate was filtered off and washed with water. After crystallisation from ethyl alcohol the *mono*-p-*nitrobenzoate* of the methyl ester of 2 : 3-dimethyl methylglucuronoside had m. p. 157° (Found : OMe, 30·1. $C_{17}H_{21}O_{10}N$ requires OMe, 31·1%).

Oxidation of the Methyl Ester of 2 : 3-*Dimethyl Methylglucuronoside with Nitric Acid*.—A solution of the methyl ester of 2 : 3-dimethyl methylglucuronoside (2·8 g.) in nitric acid (20 c.c., *d* 1·42) was heated for 1½ hours at 50° and for 5 hours at 90—95°; the solution was then diluted with water and freed from nitric acid by distillation under diminished pressure, water and finally methyl alcohol being added to facilitate this process. When all traces of solvent had been eliminated, the dry syrupy acid residue was boiled for 8 hours with 1% methyl-alcoholic hydrogen chloride (100 c.c.). After neutralisation of the mineral acid with silver carbonate, the solution was filtered and evaporated to a syrup under reduced pressure, which distilled, giving : Fraction (i) (1·1 g.), b. p. (bath temp.) 100°/0·02 mm., $n_D^{15°}$ 1·4400, $[\alpha]_D^{15°}$ + 55° in methyl alcohol (*c*, 0·4) (Found : OMe, 58·0; equiv., 98. Calc. for $C_8H_{14}O_6$: OMe, 60·2%; equiv., 103). This neutral distillate was mainly methyl *l*(+)-threodimethoxysuccinate (methyl *d*-dimethoxysuccinate), for when treated with methyl-alcoholic ammonia it gave *l*(+)-threodimethoxysuccinamide (*d*-dimethoxysuccinamide) in good yield, m. p. 288° (decomp.), $[\alpha]_D^{18°}$ + 88° in water (*c*, 1·0) (after crystallisation from methyl alcohol) (Found : OMe, 35·2. Calc. for $C_6H_{12}O_4N_2$: OMe, 35·2%). Fraction (ii) (0·4 g.), b. p. (bath temp.) 170°/0·02 mm., $n_D^{15°}$ 1·4635, $[\alpha]_D^{15°}$ + 47° in methyl alcohol (*c*, 0·5) (Found : OMe, 43·2%). This fraction crystallised partially on keeping and after removal of adhering syrup by trituration with ether the substance was purified by crystallisation from ethyl alcohol–ether; m. p. 101°. This product, which proved to the methyl ester of 2 : 3-dimethyl saccharo-γ-lactone, behaved like a lactone on titration with dilute sodium hydroxide solution (Found : OMe, 39·0. $C_9H_{14}O_7$ requires OMe, 39·8%).

2 : 3-*Dimethyl Saccharolactone Methyl Ester* (VII).—The methyl ester of 2 : 3-dimethyl methylglucuronoside (2·4 g.) was saponified by heating with barium hydroxide and the barium salt so produced was converted into the free acid, 2 : 3-dimethyl methylglucuronoside, by the addition of N-sulphuric acid (9·6 c.c.). The barium sulphate was filtered off and to the filtrate there was added sufficient sulphuric acid to make a normal solution. The solution was heated on the boiling water-bath for 30 hours to effect hydrolysis of the glycoside methyl group; it was then neutralised with barium carbonate, filtered, and concentrated to a volume of 15 c.c. To this solution of the barium salt of 2 : 3-dimethyl glucuronic acid, bromine (2 c.c.) was added and the oxidation of the reducing group was allowed to proceed at room temperature. After 4 days the excess of the bromine was removed by aeration; the solution was neutralised with silver oxide, filtered before and after treatment with hydrogen sulphide, and then evaporated to dryness under reduced pressure. The dry residue, consisting of the acid barium salt of 2 : 3-dimethyl saccharic acid, was boiled for 8 hours with 4% methyl-alcoholic hydrogen chloride (100 c.c.). The solution was cooled, neutralised with silver carbonate, filtered, and evaporated to a syrup, which distilled, giving a colourless liquid (1·0 g.), b. p. (bath temp.) 190°/0·03 mm. The distillate crystallised spontaneously and after crystallisation from ethyl alcohol–ether–light petroleum the *methyl* ester of 2 : 3-dimethyl γ-saccharolactone had m. p. 101°, $[\alpha]_D^{18°}$ + 12·0° in water (*c*, 1·0) (Found : C, 46·3; H, 6·1; OMe, 40·4; equiv., 120. $C_9H_{14}O_7$ requires C, 46·15; H, 6·0; OMe, 39·8%; equiv., 117).

A small amount of the 2 : 3-dimethyl saccharo-γ-lactone methyl ester (10—20 mg.) was heated with 0·3N-barium hydroxide (3 c.c.) for 45 minutes at 55°; the solution was neutralised with carbon dioxide and evaporated to dryness under reduced pressure. All these operations were performed in a Zeisel apparatus and a methoxyl estimation was carried out on the dry residue consisting of the barium salt of 2 : 3-dimethyl saccharic acid and barium carbonate (Found : OMe, 25·3. Calc. for the loss of one ester methyl group : OMe, 26·5%).

When treated with methyl-alcoholic ammonia, the lactone ester furnished the corresponding 2 : 3-*dimethyl saccharamide* in good yield, m. p. 156°, $[\alpha]_D^{18°}$ + 28° in water (*c*, 1·3) (after recrystallisation from ethyl alcohol) (Found : C, 40·9; H, 6·8; OMe, 25·0; N, 11·9. $C_8H_{16}O_6N_2$ requires C, 40·7; H, 6·8; OMe, 26·25; N, 11·9%).

Oxidation of 2 : 3-*Dimethyl Saccharo-γ-lactone Methyl Ester* (VII) *with Nitric Acid*.—A

solution of 2 : 3-dimethyl saccharo-γ-lactone methyl ester (0·35 g.) in nitric acid (4 c.c., *d* 1·42) was heated on the boiling water-bath for 10 hours; the solution was diluted with water and evaporated under reduced pressure to remove nitric acid (see above). The dry acidic residue was esterified by boiling for 8 hours with 1% methyl-alcoholic hydrogen chloride (30 c.c.); the solution was cooled, neutralised with silver carbonate, filtered, and concentrated to a syrup, which on distillation gave a colourless liquid (0·1 g.), b. p. (bath temp.) 100°/0·03 mm., $n_D^{18°}$ 1·4420. When this methyl ester was treated with methyl-alcoholic ammonia, there was produced *l*(+)-threodimethoxysuccinamide (*d*-dimethoxysuccinamide), m. p. and mixed m. p. 293° (decomp.), $[\alpha]_D^{18°}$ + 90° in water (*c*, 1·3) (after crystallisation from water).

Synthesis of the Methyl Ester of 2 : 3-*Dimethyl Saccharo-γ-lactone Methyl Ester from* 2 : 3-*Dimethyl Glucose.*—α-Methylglucoside was converted into 4 : 6-benzylidene α-methylglucoside according to the procedure of Irvine and Scott (J., 1913, **103**, 575) and this substance was methylated with methyl iodide and silver oxide in the presence of dry acetone; the partly methylated product was isolated by means of acetone and the methylation was completed by two more treatments with the Purdie's reagents. A solution of the 2 : 3-dimethyl 4 : 6-benzylidene α-methylglucoside (m. p. 122° after recrystallisation from ethyl alcohol–light petroleum) (8 g.) in N-sulphuric acid (150 c.c.) was heated for 7 hours on the boiling water-bath; the solution was neutralised with barium carbonate, filtered, and evaporated to dryness under reduced pressure. The syrupy residue consisting of 2 : 3-dimethyl glucose was converted into the methylglucoside by boiling with 1% methyl-alcoholic hydrogen chloride. The 2 : 3-dimethyl methylglucoside distilled as a colourless liquid (4·5 g.), b. p. (bath temp.) 165—170°/0·03 mm., $n_D^{19°}$ 1·4720 (Found: OMe, 41·0. Calc. for $C_9H_{18}O_6$: OMe, 41·9%).

A solution of 2 : 3-dimethyl methylglucoside (2·1 g.) in nitric acid (20 c.c., *d* 1·42) was heated for 1 hour at 60° and for 2 hours at 90°, and the solution was then diluted with water and freed from nitric acid as in previous cases. The dry residue was esterified by boiling for 8 hours with 1% methyl-alcoholic hydrogen chloride (50 c.c.). The methyl esters were isolated in the usual way and distilled, giving: Fraction (I), methyl *l*(+)-threodimethoxysuccinate (1·2 g.), b. p. (bath temp.) 100°/0·01 mm., $n_D^{20°}$ 1·4390. Fraction (II) (0·2 g.), b. p. (bath temp.) 150—160°/0·01 mm. This second fraction crystallised spontaneously and after recrystallisation from ethyl alcohol–ether–light petroleum the methyl ester of 2 : 3-dimethyl saccharo-γ-lactone had m. p. 101° alone or in admixture with the specimen previously prepared from the methyl ester of 2 : 3-dimethyl methylglucuronoside; $[\alpha]_D^{22°}$ + 14° (initial value in water, *c*, 3·1); + 20·6° (4 days); + 23·6 (6 days); + 26° (8 days); + 27·7° (10 days) (Found: C, 46·2; H, 6·2; OMe, 40·0. Calc. for $C_9H_{14}O_7$: C, 46·15; H, 6·0; OMe, 39·8%).

An unsuccessful attempt was made to prepare 2 : 3-dimethyl saccharo-1 : 4-lactone methyl ester from 2 : 3 : 6-trimethyl δ-gluconolactone (Haworth, Peat, and Whetstone, J., 1938, 1975) {m. p. 85°; $[\alpha]_D^{20°}$ + 90°, changing to + 35° equilibrium value in water, *c*, 2·5 (after recrystallisation from ether)} by oxidation with nitric acid. The main product of the reaction was *l*(+)-threodimethoxysuccinic acid (*d*-dimethoxysuccinic acid).

2 : 3 : 5-*Trimethyl Saccharo-γ-lactone Methyl Ester* (VIII).—2 : 3-Dimethyl saccharolactone methyl ester (50 mg.) was methylated once with Purdie's reagents and there was isolated by means of acetone, crystalline 2 : 3 : 5-trimethyl saccharo-γ-lactone methyl ester (50 mg.), which separated well from ethyl alcohol–ether; m. p. 78° alone or in admixture with authentic 2 : 3 : 5-trimethyl saccharo-γ-lactone methyl ester prepared from 2 : 3 : 5-trimethyl methylglucofuranoside (unpublished results); $[\alpha]_D^{20°}$ − 10° in water (*c*, 2·0) (Found: OMe, 49·7. $C_{10}H_{16}O_7$ requires OMe, 50·0%).

Examination of the Light-petroleum-soluble Glycosides (C).—This mixture of methylated glycosides was slowly distilled through a fractionating column, giving:

Fraction.	B. p. (bath temp.).	Pressure, mm.	Weight, g.	$n_D^{15°}$.	% OMe.
D	105°	0·07	3·4	1·4370	58·0
E	105—110	0·02	1·02	1·4450	56·0
F	110—130	0·02	4·26	1·4475	56·2
G	130—145	0·02	0·6	1·4530	51·4

There remained a residue (1·7 g.; $n_D^{17°}$ 1·4725) which crystallised on cooling; it consisted mainly of the α- and the β-form of 2 : 4-dimethyl methylgalactoside.

Fraction D was slowly redistilled and when the refractive index of the contents of the flask reached that of fraction E, the latter was added and the distillation was continued. This process was repeated until eventually the whole of the material from the first distillation had been redistilled and in this way there were obtained:

Fraction.	B. p. (bath temp.).	Pressure, mm.	Weight, g.	$n_D^{18°}$.	% OMe.
H	90–95°	0·01	3·08	1·4350	58·2
J	95–105	0·01	1·04	1·4455	56·4
K	105–120	0·08	4·3	1·4467	56·2
L	above 120	0·01	0·54	1·4510	55·3

It is clear that this second fractional distillation effects little or no improvement in the separation of the glycosides.

Examination of Fraction H. The Identification of 2 : 3 : 5-*Trimethyl* l-*Arabinose* (XIII) *and* 2 : 3 : 4-*Trimethyl* l-*Rhamnose* (XII).—Fraction (H) was again distilled and collected in two approximately equal fractions, but as before no separation could be effected; both fractions had the same b. p. (90—95°/0·01 mm.), refractive index ($n_D^{18°}$ 1·4350) and methoxyl content (OMe, 58·1%) (Calc. for an equimolecular mixture of trimethyl methylarabinoside and trimethyl methylrhamnoside: OMe, 58·0%). The first fraction, however, had $[\alpha]_D^{20°}$ — 62° in water (*c*, 1·1) and the second had $[\alpha]_D^{20°}$ — 22° in water (*c*, 1·0), but since this difference in rotation was probably due to partial separation of the two glycosides into α- and β-forms and not a real separation of trimethyl methylrhamnoside from the trimethyl methylarabinoside, the two fractions were combined and the material (3·0 g.) was heated with 0·1N-sulphuric acid (100 c.c.) on the boiling water-bath for 9½ hours. The rate of hydrolysis as shown by polarimetric observations suggested that one of the constituents of the mixture was a furanoside: $[\alpha]_D$ — 60° (initial value); — 48° (3 hours); — 35·5° (5 hours); — 27° (6 hours); — 26° (7 hours); — 27° (8½ hours) (const. for a further hour). The solution was neutralised with barium carbonate, filtered, and evaporated to dryness. The syrupy reducing product thus obtained gave on distillation: Fraction (i) (0·54 g.), b. p. (bath temp.) 110—115°/0·08 mm., $n_D^{20°}$ 1·4390—1·4460, $[\alpha]_D^{20°}$ — 37° in water (*c*, 1·4) (Found: OMe, 52·4%). Fraction (ii) (2·2 g.), b. p. (bath temp.) 115°/0·08 mm., $n_D^{20°}$ 1·4490, $[\alpha]_D^{20°}$ — 25° in water (*c*, 0·9) (Found: OMe, 45·5%). Fraction (i) reduced Fehling's solution, but it still contained some unhydrolysed methylated glycoside, because when it was re-treated with 0·1N-sulphuric acid for 19 hours on the boiling water-bath a change in rotation was observed and the product, isolated as before, had b. p. (bath temp.) 110°/0·05 mm., $n_D^{21°}$ 1·4476, $[\alpha]_D^{21°}$ — 21° in water (*c*, 0·6) (Found: OMe, 48·3%). Fraction (ii), however, appeared to be completely hydrolysed, because it underwent no change even when heated on the boiling water-bath with N-sulphuric acid.

In view of the impossibility of separating this constant-boiling mixture of 2 : 3 : 5-trimethyl methylarabinoside and 2 : 3 : 4-trimethyl methylrhamnoside by preferential hydrolysis, fraction (i) was completely hydrolysed with N-sulphuric acid and the reducing product obtained was combined with the reducing methylated sugar of fraction (ii).

A small amount of this combined mixture of reducing methylated sugars, when treated with boiling ethyl-alcoholic aniline, furnished an anilide which crystallised on keeping. The crystals were freed from adhering syrup by trituration with light petroleum and recrystallisation from the same solvent gave 2 : 3 : 4-trimethyl rhamnose anilide, m. p. 111°. A solution of another portion of the combined mixture of reducing methylated sugars (1·7 g.) in water (15 c.c.) was treated with bromine (2 c.c.) for 2 days at room temperature and for 2 hours at 30°. The solution was freed from bromine by aeration, neutralised with silver oxide, filtered before and after treatment with hydrogen sulphide, and then evaporated to dryness under diminished pressure, whereby there was obtained a syrup, which distilled, giving a colourless mobile liquid (1·3 g.), b. p. (bath temp.) 100°/0·05 mm., $n_D^{19°}$ 1·4470, $[\alpha]_D^{16°}$ — 61° (initial value in water, *c* 0·8), changing in 17 hours to — 57° (Found: OMe, 46·5%). Treatment of this lactone mixture with methyl-alcoholic ammonia for 12 hours at — 5° gave the amide of 2 : 3 : 5-trimethyl *l*-arabonic acid, m. p. and mixed m. p. 138°, $[\alpha]_D^{18°}$ + 21° in ethyl alcohol (*c*, 0·9) (after recrystallisation from acetone) (Found: C, 46·5; H, 7·9; N, 6·8; OMe, 44·9. Calc. for $C_8H_{17}O_5N$: C, 46·4; H, 8·3; N, 6·8; OMe, 44·9%). When the lactone mixture was allowed to react with phenylhydrazine in the usual way, it afforded the phenylhydrazide of 2 : 3 : 4-trimethyl *l*-rhamnonic acid, m. p. and mixed m. p. 177° (after crystallisation from ethyl alcohol–ether) (Found: C, 57·6; H, 7·6; N, 9·1; OMe, 29·6. Calc. for $C_{15}H_{24}O_5N_2$: C, 57·7; H, 7·8; N, 9·0; OMe, 29·8%).

Examination of Fraction K. The Identification of 2 : 3 : 4 : 6-*Tetramethyl Galactose* (XX) *and* 2 : 5-*Dimethyl Arabinose* (XIX).—Fraction (K) was slowly distilled and separated into two fractions, which were found to be identical, b. p. (bath temp.) 110°/0·10 mm., $n_D^{21°}$ 1·4470, $[\alpha]_D^{18°}$ + 34° in water (*c*, 1·0) (Found: OMe, 56·1. Calc. for an equimolecular mixture of tetramethyl methylgalactoside and dimethyl methylarabinoside: OMe, 56·0%). The two fractions were combined and a solution of the mixture (4·1 g.) in 0·1N-sulphuric acid was heated on the

boiling water-bath: $[\alpha]_D$ + 33° (initial value); + 43·5° (1 hour); + 54° (2 hours); + 60·5° (3 hours); + 64° (4 hours); + 65·5° (5 hours); + 66° (6 hours); + 66·3° (7 hours; constant for a further 2 hours). The solution was then neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure. The product, a syrup which reduced Fehling's solution actively, gave on distillation: Fraction (i) (1·4 g.), b. p. (bath temp.), 115—120°/0·10 mm., $n_D^{20°}$ 1·4482—1·4510, $[\alpha]_D^{20°}$ + 129° in water (*c*, 0·7) (Found: OMe, 58·8. Calc. for tetramethyl methylgalactoside: OMe, 61·9%). Fraction (ii) (0·4 g.), b. p. (bath temp.) 120—140°/0·10 mm., $n_D^{20°}$ 1·4520—1·4605, $[\alpha]_D^{20°}$ + 83° in water (*c*, 0·6) (Found: OMe, 52·5%). Fraction (iii) (2·0 g.), b. p. (bath temp.) 140°/0·10 mm., $n_D^{21°}$ 1·4635, $[\alpha]_D^{20°}$ + 41·2° in water (*c*, 0·6) (Found: OMe, 44·0. Calc. for an equimolecular mixture of tetramethyl galactose and 2 : 5-dimethyl arabinose: OMe, 44·9%).

Fraction (i) was rehydrolysed by heating with 0·1N-sulphuric acid for 9 hours on the boiling water-bath; the product, isolated as in previous cases, was distilled, giving: Fraction (a) (tetramethyl methylgalactoside) (0·72 g.), b. p. (bath temp.) 100°/0·01 mm., $n_D^{22°}$ 1·4480, $[\alpha]_D^{20°}$ + 149° in water (*c*, 0·6) (Found: OMe, 59·5. Calc. for $C_{11}H_{22}O_6$: OMe, 61·9%). Fraction (b) (0·48 g.), b. p. (bath temp.) 100°/0·07 mm., $n_D^{22°}$ 1·4613, $[\alpha]_D^{20°}$ + 113° in water (*c*, 0·7) (Found: OMe, 52·7%).

A solution of fraction (a) (0·7 g.) in N-sulphuric acid (25 c.c.), was heated on the boiling water-bath for 10 hours: $[\alpha]_D$ + 152° (initial value); + 137·5° (1 hour); + 126° (2 hours); + 118° (3 hours); + 114° (4 hours); + 111° (5 hours); + 108·5° (6 hours); + 107° (7 hours); + 106° (8 hours); + 105° (10 hours, constant value). The solution was neutralised with barium carbonate, filtered, and evaporated to dryness to give a syrup (0·6 g.), which distilled, b. p. (bath temp.) 130°/0·03 mm., $n_D^{20°}$ 1·4625 (Found: OMe, 51·6%). The distillate crystallised on keeping and after recrystallisation from ether–light petroleum the 2 : 3 : 4 : 6-tetramethyl galactose had m. p. and mixed m. p. 75° (Found: C, 51·0; H, 8·2; OMe, 52·3. Calc. for $C_{10}H_{20}O_6$: C, 50·9; H, 8·6; OMe, 52·5%).

The fractions (ii), (iii), and (b), all of which reduced boiling Fehling's solution, were combined and completely hydrolysed by heating on the boiling water-bath with N-sulphuric acid (50 c.c.). The mixture of reducing methylated sugars produced in this way was isolated as previously described and distilled, giving 2·5 g., b. p. (bath temp.) 135°/0·04 mm., $n_D^{19°}$ 1·4660, $[\alpha]_D^{20°}$ + 51·5° in water (*c*, 0·7) (Found: OMe, 44·4%). The distillate was divided into three parts (c, 1·0 g.), (d, 0·3 g.) and (e, 1·2 g.).

The first portion (c) (1·0 g.) was completely methylated with Purdie's reagents (two treatments) and there was obtained a liquid (0·9 g.), b. p. (bath temp.) 95°/0·05 mm., $n_D^{17°}$ 1·4390, $[\alpha]_D^{18°}$ + 5° in water (*c*, 1·0) (Found: OMe, 61·0%). This mixture of methylated glycosides was completely hydrolysed by heating with 0·2N-sulphuric acid (20 c.c.) until the rotation became constant. The product, isolated as previously described (0·8 g.) (Found: OMe, 45·7%), was dissolved in water (5 c.c.) and treated with bromine (1 c.c.) at room temperature until the oxidation was complete. The syrupy lactone mixture isolated as in previous cases distilled as a colourless, fairly mobile syrup, b. p. (bath temp.) 140°/0·07 mm., $[\alpha]_D^{20°}$ + 105° (initial value in water, *c* 0·9); + 18·5° (after 14 hours); + 21° (after 38 hours) (Found: OMe, 50·0%). When this lactone mixture was boiled with ethereal phenylhydrazine for 15 minutes and then heated (after removal of solvent) for 2 hours at 95°, there was obtained the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl galactonic acid, m. p. and mixed m. p. 138° (Found: C, 56·3; H, 7·7; N, 8·3; OMe, 37·0. Calc. for $C_{16}H_{26}O_6N_2$: C, 56·1; H, 7·7; N, 8·2; OMe, 36·3%). Treatment of the lactone mixture with methyl-alcoholic ammonia gave the amide of 2 : 3 : 5-trimethyl *l*-arabonic acid, m. p. and mixed m. p. 138° (after recrystallisation from acetone–ether).

The second portion (d) (0·3 g.) was boiled for 3 hours with ethyl-alcoholic aniline (0·2 g. in 5 c.c.); removal of half of the solvent, followed by the addition of ether (5 c.c.), gave the crystalline anilide of 2 : 3 : 4 : 6-tetramethyl galactose, which separated well from ethyl alcohol; m. p. 192° alone or in admixture with an authentic specimen (Found: N, 4·7; OMe, 40·9. Calc. for $C_{16}H_{25}O_5N$: N, 4·5; OMe, 39·9%).

A solution of the third portion (e) (1·2 g.) in water (10 c.c.) was treated with bromine (2 c.c.) for 24 hours at room temperature and for 5 hours at 35°. The excess of the bromine was removed, and the lactone, isolated as above, was distilled, giving 0·9 g., b. p. (bath temp.) 135—140°/0·05 mm., $n_D^{20°}$ 1·4570, $[\alpha]_D^{20°}$ + 54° (initial value in water, *c* 0·7); + 9·5° (6 hours); − 1·5° (10 hours); − 4·2° (11 hours); − 8·5° (23 hours, constant for 24 hours) (Found: OMe, 44·8%). This lactone mixture furnished the amide of 2 : 5-dimethyl *l*-arabonic acid on treatment with methyl-alcoholic ammonia for 12 hours at − 5°. After recrystallisation from ethyl alcohol–ether the amide had $[\alpha]_D^{18°}$ + 38° in water (*c*, 1·4), m. p. 132° alone or in admixture with

a pure specimen prepared from heptamethyl 3-*d*-galactosido-*l*-arabofuranose (J., 1939, 744) (Found: C, 43·6; H, 7·5; N, 7·2; OMe, 31·8. Calc. for $C_7H_{15}O_5N$: C, 43·5; H, 7·8; N, 7·25; OMe, 32·2%).

A solution of the lactone mixture (0·1 g.) in ether (2 c.c.) was treated with phenylhydrazine (0·06 g.) at room temperature, and after ½ hour a crystal of the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl galactonic acid was added. The separation of this phenylhydrazide from the solution in plates was subjected to careful observation and when the second type of crystals (rosettes of needles of the phenylhydrazide of 2 : 5-dimethyl *l*-arabonic acid) made their appearance, the liquid was decanted from the crystals, which were washed with ether. Purification of the crystals by recrystallisation from ethyl alcohol–ether gave the phenylhydrazide of 2 : 3 : 4 : 6-tetramethyl galactonic acid, m. p. and mixed m. p. 138°. On allowing the solution decanted from the crystals to stand with the ethereal washings of the latter (3 c.c.) at room temperature for a further 12 hours, the phenylhydrazide of 2 : 5-dimethyl *l*-arabonic acid separated in needles, m. p. and mixed m. p. 163° (after recrystallisation from ethyl alcohol–ether) (Found: C, 55·0; H, 7·1; N, 10·0; OMe, 22·0. Calc. for $C_{13}H_{20}O_5N_2$: C, 54·9; H, 7·1; N, 9·9; OMe, 21·8%).

When a mixture of methylated glycosides (2·2 g.) corresponding to fraction H (obtained from another sample of methylated arabic acid) was hydrolysed by heating with 0·1N-sulphuric acid on the boiling water-bath, it showed $[\alpha]_D$ − 47° (initial value); − 44° (1·25 hours); − 35° (2 hours); − 30° (4 hours); − 24° (6·5 hours); − 19·5° (8 hours); − 18·5° (9 hours); − 16·5° (11·5 hours); − 14° (15·5 hours); − 13·5° (20 hours). The hydrolysis was now complete, for when the strength of the sulphuric acid was increased to N, the solution showed no change in specific rotation after being heated for a further 2 hours on the boiling water-bath. After removal of the mineral acid with barium carbonate, and the solvent by evaporation under diminished pressure, there was obtained a syrupy mixture of reducing methylated sugars, which distilled as a colourless liquid (1·4 g.), b. p. (bath temp.) 125—130°/0·01 mm., $n_D^{20°}$ 1·4550, $[\alpha]_D^{18°}$ − 14·5° in water (*c*, 1·6) (Found: OMe, 45·5%). A solution of this mixture of sugars (1·0 g.) in water (10 c.c.) was oxidised with bromine (1 c.c.) for 2 days at room temperature in the presence of lead carbonate (2 g.). The solution was freed from bromine by aeration, filtered before and after treatment with hydrogen sulphide, and concentrated under reduced pressure to remove hydrogen sulphide. The solution was then neutralised with silver oxide, filtered, and worked up in the usual way for a bromine oxidation to give the mixture of lactones, which distilled as a colourless mobile liquid (0·6 g.), b. p. (bath temp.) 100—110°/0·08 mm., $n_D^{16°}$ 1·4533 (Found: OMe, 45·8%); $[\alpha]_D^{18°}$ − 68° (initial value in water, *c* 1·3); − 52° (after 4 days); − 46° (19 days); − 44·5° (29 days). Calculated for an equimolecular mixture of 2 : 3 : 4-trimethyl *l*-rhamnose and 2 : 3 : 5-trimethyl *l*-arabinose, OMe, 46·6%, and on the assumption that the rotations of these two compounds are − 39·5° (Baker and Haworth, J., 1925, **127**, 365) and + 24° (Haworth, Hirst, and Miller, J., 1929, 2469) respectively, the rotation of the mixture should be *ca.* − 6°. Calculated for the corresponding mixture of lactones, OMe, 47·2%; $[\alpha]_D$ − 88°, assuming that the rotations of 2 : 3 : 5-trimethyl γ-arabonolactone and 2 : 3 : 4-trimethyl δ-rhamnonolactone are − 44° (Drew, Goodyear, and Haworth, J., 1927, 1237) and − 130° (Haworth, Hirst, and Miller, *loc. cit.*) respectively.

Similarly, when a solution of the mixture of glycosides (2·1 g.) (corresponding to fraction K, see above) in N-sulphuric acid (50 c.c.) was heated on the boiling water-bath, it showed $[\alpha]_D$ + 52° (initial value); + 75° (after 2·5 hours); + 69° (5 hours); + 65·5° (8½ hours) (constant value). The mixture of 2 : 3 : 4 : 6-tetramethyl galactose and 2 : 5-dimethyl *l*-arabinose obtained from this solution, in the manner previously described, distilled as a colourless liquid (1·7 g.), b. p. (bath temp.) 120°/0·03 mm., $n_D^{16°}$ 1·4670, $[\alpha]_D$ + 72° (in water, *c* 1·1) (Found: OMe, 46·0%). The mixture of lactones prepared from this mixture of reducing methylated sugars by a bromine oxidation in the presence of lead carbonate (see above) had b. p. (bath temp.) 130°/0·03 mm., $n_D^{19°}$ 1·4620 (Found: OMe, 46·2%); $[\alpha]_D^{18°}$ + 76° (initial value in water, *c* 2·0); + 60·5° (7·25 hours); + 33·5° (3·75 hours); + 17·5° (6·25 hours); + 5·5° (16 hours); + 7° (40 hours); + 11° (192 hours). Calculated for an equimolecular mixture of 2 : 3 : 4 : 6-tetramethyl galactose and 2 : 5-dimethyl *l*-arabinose, OMe, 45·0%, and the calculated value for the methoxyl content of the lactones is 45·3% and its rotation is $[\alpha]_D$ *ca.* + 70°, assuming that the rotation of 2 : 3 : 4 : 6-tetramethyl δ-galactonolactone is + 166·5° (Drew, Goodyear, and Haworth, *loc. cit.*) and that of 2 : 5-dimethyl γ-*l*-arabonolactone is − 60° (Smith, J., 1939, 744).

Hydrolysis of heptamethyl 3-galactosido-*l*-arabofuranose (Smith, J., 1939, 744) with boiling 2% methyl-alcoholic hydrogen chloride furnished a mixture of methylated glycosides which had b. p. (bath temp.) 120°/0·04 mm., $n_D^{21°}$ 1·4510, $[\alpha]_D^{20°}$ + 50° in water (*c*, 1·7) (Found: OMe,

55·0%). The corresponding mixture of reducing methylated sugars, prepared by treating the mixture of glycosides with N-sulphuric acid for 16 hours at 95°, had b. p. (bath temp.) 145°/0·03 mm., $n_D^{16°}$ 1·4690, $[\alpha]_D^{20°}$ + 72° in water (*c*, 1·2) (Found : OMe, 44·0%). When comparing the properties of this mixture of glycosides and the mixture of reducing methylated sugars with those derived from fraction K (see above), it must be borne in mind that the arabinose moiety in the heptamethyl 3-galactosido-*l*-arabinose may not be all in the furanoside form but may also be partly in the pyranoside form, with the result that the methylated disaccharide will furnish some 2 : 4-dimethyl arabinose derivatives in addition to 2 : 5-dimethyl derivatives; these figures are therefore recorded with reserve.

Examination of Fraction J.—When a solution of this mobile liquid (1·0 g.) in 0·7N-sulphuric acid (30 c.c.) was heated on the boiling water-bath, it showed $[\alpha]_D$ + 39° (initial value); + 53° (3 hours); + 49° (5 hours) (constant for 1½ hours). After neutralisation of the sulphuric acid with barium carbonate, the solution was filtered and evaporated under reduced pressure to a syrup, which distilled as a colourless liquid, b. p. (bath temp.) 130—150°/0·02 mm., $n_D^{23°}$ 1·4570—1·4670, $[\alpha]_D^{20°}$ + 59° in water (*c*, 1·3) (Found : OMe, 45·2%).

Treatment of this syrupy mixture of reducing methylated sugars (50 mg.) with aniline (30 mg.) in boiling ethyl alcohol (1·5 c.c.) for 2 hours gave the anilide of 2 : 3 : 4 : 6-tetramethyl galactose, m. p. and mixed m. p. 192° (after recrystallisation from ethyl alcohol–ether). No other crystalline anilide could be obtained from the mother-liquors.

A solution of the rest of the mixture of reducing methylated sugars in water (15 c.c.) was oxidised with bromine (0·5 c.c.) at room temperature for 3 days. The excess of the bromine was removed by aeration. The solution was neutralised with silver oxide, filtered, and treated with hydrogen sulphide. The liquid, which still contained colloidal silver sulphide, was decanted from the precipitated silver sulphide and the latter was washed several times by decantation. The decanted liquid and the washings were combined and evaporated to a syrup under diminished pressure. The product was extracted with acetone and to the acetone solution excess of ether was added. A small amount of flocculent material was filtered off and on removal of the solvent there was obtained a syrup, which distilled as a colourless mobile liquid (0·7 g.), b. p. (bath temp.) 140°/0·04 mm., $n_D^{20°}$ 1·4590, $[\alpha]_D^{21°}$ + 61° (initial value in water, *c* 1·5); + 38·5° (after 1½ hours); + 2° (5½ hours); ± 0·0° (8 hours); − 1° (11 hours) (Found : OMe, 46·5%).

Treatment of the mixture of methylated lactones (0·1 g.) with phenylhydrazine (0·06 g.) for 10 minutes in boiling ethereal solution and then for 1 hour at 95° in the absence of solvent, gave a pale yellow syrup, which crystallised on trituration with ether. Recrystallisation of the product from ethyl alcohol–ether gave in good yield the phenylhydrazide of 2 : 5-dimethyl *l*-arabonic acid, m. p. and mixed m. p. 163°.

When the lactone mixture was allowed to react with methyl-alcoholic ammonia for 2 days at − 5°, there was obtained an amide which crystallised on removal of the solvent. The crystals were filtered off and recrystallised from ethyl alcohol–acetone to give the amide of 2 : 5-dimethyl *l*-arabonic acid, m. p. and mixed m. p. 132°. Extraction of the syrup obtained from the mother-liquors with ether gave a small amount of the amide of 2 : 3 : 4 : 6-tetramethyl galactonic acid, m. p. and mixed m. p. 122° (after recrystallisation from ether–light petroleum).

Examination of Fraction L.—Complete hydrolysis of this fraction by heating it for 10 hours on the boiling water-bath with 0·5N-sulphuric acid gave a mixture of reducing methylated sugars which had $[\alpha]_D^{20°}$ + 58° in water (*c*, 1·4) (Found : OMe, 37·5%).

Oxidation of this mixture of reducing methylated sugars with bromine as in previous cases gave the corresponding mixture of lactones, which distilled as a colourless liquid, b. p. (bath temp.) 145°/0·05 mm., $n_D^{20°}$ 1·4640, $[\alpha]_D^{18°}$ + 51° (initial value in water, *c* 1·0); + 42° (1 hour); + 16·5° (3½ hours); + 3° (6½ hours); − 2° (10 hours); − 4° (20½ hours); + 12° (27 days). The distillate reacted acid to Congo-paper (Found : OMe, 40·9%).

When this mixture of methylated lactones was treated with methyl-alcoholic ammonia for 2 days at − 5°, it gave mainly the amide of 2 : 5-dimethyl-*l*-arabonic acid, m. p. and mixed m. p. 132°. A small amount of an unidentified substance was isolated from the mother-liquors, m. p. *ca.* 158° (after recrystallisation from ethyl alcohol–ether).

Treatment of the mixture of methylated lactones with phenylhydrazine afforded in good yield the phenylhydrazide of 2 : 5-dimethyl *l*-arabonic acid, m. p. and mixed m. p. 163° (after recrystallisation from ethyl alcohol–ether).

Examination of the Light-petroleum-insoluble Fraction R. Identification of 2 : 4-Dimethyl Galactose (XXV).—That portion of the methylated glycosides (B) (14·3 g.) insoluble in light petroleum crystallised on keeping and after trituration with ether–light petroleum to remove adhering syrup, the residue was crystallised from acetone–light petroleum, giving 2 : 4-dimethyl

β-methylgalactoside, m. p. and mixed m. p. 166° (Found: OMe, 41·5. Calc. for $C_9H_{18}O_6$: OMe, 41·9%). The syrup obtained on removal of the solvent from the mother-liquors was boiled for 8 hours with 2% methyl-alcoholic hydrogen chloride (200 c.c.); the solution was cooled, neutralised with silver carbonate, filtered, and evaporated under reduced pressure, giving a syrup (13·2 g.) (Found: OMe, 41·0%), which crystallised on keeping. After recrystallisation of the 2 : 4-dimethyl α-methylgalactoside, obtained in this way, from acetone–light petroleum it had m. p. and mixed m. p. 105°, $[\alpha]_D^{18°}$ + 143° in water (*c*, 1·1) (Found: OMe, 42·0. Calc. for $C_9H_{18}O_6$: OMe, 41·9%).

Solutions of the α- and of the β-form of 2 : 4-dimethyl methylgalactoside in N-sulphuric acid were heated on the boiling water-bath until the specific rotation became constant. Each was neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure. In both cases 2 : 4-dimethyl galactose was obtained as a syrup, which crystallised as the monohydrate when triturated with a little water or on exposure to the air. It had m. p. and mixed m. p. 103°, $[\alpha]_D^{18°}$ + 86° (equilibrium value in water, *c* 1·1) after crystallisation from ethyl alcohol–acetone–ether (Found: OMe, 27·2. Calc. for $C_8H_{18}O_7$: OMe, 27·4%).

A solution of 2 : 4-dimethyl galactose (from which the water of crystallisation had been removed by heating in a vacuum at 110°) in 1% methyl-alcoholic hydrogen chloride showed: $[\alpha]_D^{18°}$ + 55° (initial value); + 57° after 1 hour); + 66° (6 hours); + 77° (10 hours); + 86° (15 hours); + 93° (20 hours); + 105° (30 hours); + 110° (35 hours); + 117° (45 hours); + 120° (60 hours); + 128° (84 hours); + 131° (108 hours); + 135° (133 hours) (constant value). Neutralisation of the mineral acid with silver carbonate, followed by removal of the solvent, gave 2 : 4-dimethyl α-methylgalactopyranoside, m. p. and mixed m. p. 164°, $[\alpha]_D^{18°}$ + 143° in water (*c*, 1·0) (after recrystallisation from acetone–light petroleum).

A solution of the 2 : 4-dimethyl galactose monohydrate (1·0 g.) in water (15 c.c.) was treated with bromine (2 c.c.) at room temperature until the solution no longer reduced Fehling's solution. The solution was freed from excess of the bromine by aeration, neutralised with silver oxide, filtered before and after treatment with hydrogen sulphide, and evaporated to dryness under reduced pressure. The syrupy product was purified by extraction with acetone–ether and distilled in a high vacuum, giving 2 : 4-dimethyl δ-galactonolactone (0·6 g.), which separated well from dry acetone; m. p. 113°, $[\alpha]_D^{18°}$ + 158° (after 5 mins. in water, *c* 0·5). (This δ-lactone changes to a syrup unless it is kept quite dry.) (Found: OMe, 29·8. Calc. for $C_8H_{14}O_6$: OMe, 30·1%). When treated with phenylhydrazine, the 2 : 4-dimethyl δ-galactonolactone yielded the phenylhydrazide of 2 : 4-dimethyl galactonic acid, m. p. and mixed m. p. 183° (after recrystallisation from ethyl alcohol–ether), and with methyl-alcoholic ammonia the 2 : 4-dimethyl δ-galactonolactone gave the corresponding amide, m. p. and mixed m. p. 167° (after recrystallisation from ethyl alcohol).

The presence of 2 : 5-dimethyl methylarabinoside in the mixture of the light-petroleum-soluble methylated glycosides (4·4 g.) obtained from another specimen of methylated arabic acid (16·5 g.) has also been established in the following manner. The mixture of methylated glycosides was completely hydrolysed by heating for 10 hours with N-sulphuric acid (50 c.c.) on the boiling water-bath. The solution was neutralised with barium carbonate, filtered, and evaporated to a syrup under diminished pressure. This reducing syrup was extracted with boiling light petroleum until there remained 1·1 g. of syrup (Found: OMe, 36·6. Calc. for dimethyl arabinose: OMe, 34·8%). The extraction with light petroleum was repeated several times until the residue amounted to 0·72 g. This product had $[\alpha]_D^{18°}$ − 2° in water (*c*, 1·0) (Found: OMe, 34·1%). The reducing methylated sugar (0·7 g.) was then converted into the corresponding methylfuranoside by means of 1% methyl-alcoholic hydrogen chloride (25 c.c.) at room temperature: $[\alpha]_D$ − 18° (initial value); + 20° (1 hour); + 37°·(2½ hours); + 31° (6 hours); ± 0° (14 hours); − 15° (20 hours); − 30° (28 hours); − 41° (40 hours); − 46° (50 hours); − 51° (70 hours); − 52° (90 hours, constant for a further 24 hours). The solution ($[\alpha]_D$ − 52°) was neutralised with silver carbonate, filtered, and evaporated to a syrup, which was distilled, giving 0·54 g., b. p. (bath temp.) 110°/0·03 mm., $n_D^{19°}$ 1·4475, $[\alpha]_D^{18°}$ − 60° in water (*c*, 0·9) (Found: OMe, 47·3. Calc. for $C_8H_{16}O_6$: OMe, 48·5%). This furanoside was hydrolysed by heating with 0·2N-sulphuric acid for 4 hours on the boiling water-bath; the reducing sugar was isolated as in previous cases and converted by means of bromine into the corresponding lactone, which was distilled in a high vacuum, giving a colourless liquid, $[\alpha]_D^{20°}$ − 45° (initial value in water, *c* 1·0) (Found: OMe, 33·6%). The distillate crystallised on keeping and after recrystallisation from ether it gave pure 2 : 5-dimethyl-γ-arabonolactone, m. p. and mixed m. p. 60°, $[\alpha]_D^{25°}$ − 58° (initial value in water, *c* 1·0) (Found: OMe, 35·1. Calc. for $C_7H_{12}O_5$: OMe, 35·2%).

Isolation of l-*Rhamnose from Arabic Acid.*—A mixture of the reducing sugars, consisting of *l*-arabinose, *l*-rhamnose, and 3-galactosido-*l*-arabinose, obtained from arabic acid by autohydrolysis was freed from as much of the *l*-arabinose as possible (see Part I, J., 1939, 744). A solution of the syrup obtained from the mother-liquors in a small quantity of methyl alcohol was then poured into a dish and allowed to evaporate slowly in the air. After keeping at room temperature for about 18 months the large crystals of *l*-rhamnose hydrate which had separated were picked out and freed from the adhering thin syrup by a quick washing with methyl alcohol. These crystals were dissolved in a small volume of hot ethyl alcohol and a few drops of water were added; on cooling, *l*-rhamnose monohydrate separated, m. p. 101°, $[\alpha]_D^{18°} + 10°$ (equilibrium value in water) (*c*, 1·0) (Found: C, 39·8; H, 7·8. Calc. for $C_6H_{12}O_5,H_2O$: C, 39·6; H, 7·7%).

The Phenylhydrazide of 2 : 3 : 5-*Trimethyl* l-*Rhamnonic Acid.*—The compound was prepared for reference purposes by treating the crystalline 2 : 3 : 5-trimethyl γ-*l*-rhamnonolactone (50 mg.) with phenylhydrazine (40 mg.) in boiling ethereal solution for 30 minutes and then for 3 hours at 90° in the absence of solvent. Trituration of the crystalline residue with ether, followed by recrystallisation from ethyl alcohol–ether–light petroleum, gave the *phenylhydrazide* of 2 : 3 : 5-trimethyl *l*-rhamnonic acid, m. p. 160° (Found: C, 57·9; H, 7·85; OMe, 29·7. $C_{15}H_{24}O_5N_2$ requires C, 57·7; H, 7·7; OMe, 29·8%).

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