229. *Pectic Substances. Part VI. The Structure of the Araban from* Arachis Hypogea.

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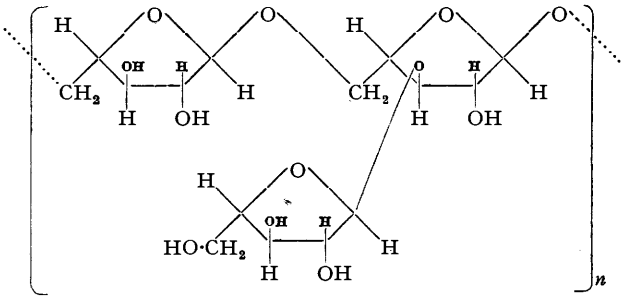
The constitution of the araban component of the pectic material present in the peanut (*Arachis Hypogea*) has been further investigated. On hydrolysis of the methylated araban, trimethyl methyl-*l*-arabofuranoside, 2 : 3-dimethyl methyl-*l*-arabinoside, and a monomethyl methyl-*l*-arabinoside were isolated in the approximate proportions 1 : 1 : 1. The monomethyl arabinose has now been identified as the 2-methyl derivative, and no other monomethyl *l*-arabinose could be detected. The bearing of these results on the structure of araban is discussed.

Arabans isolated from several sources of pectin have already been examined, and in all cases it has been demonstrated that on hydrolysis the methylated polysaccharide gave rise to three derivatives of arabinose in approximately equal proportions (Hirst and Jones, *J.*, 1938, 496; 1939, 454, 456, 1865). These arabinose derivatives were identified as 2 : 3 : 5-trimethyl *l*-arabofuranose, 2 : 3-dimethyl *l*-arabinose, and a monomethyl *l*-arabinose which was provisionally identified as 3-methyl *l*-arabinose. The identification of this substance was dependent upon the following observations: (1) The sugar had no methoxyl group on C_5, since on acidic hydrolysis of the glycoside it gave a derivative of *l*-arabopyranose characterised by its high positive rotation; (2) it had a hydroxyl group on C_4, since on oxidation it gave a furano-lactone showing a negative rotation and a characteristic slow rate of hydrolysis. Moreover, the rate of hydrolysis of the original araban indicated that all the arabinose components were present in the furanose form and therefore that the hydroxyl group on C_4 was engaged in ring formation and could not be replaced by a methoxyl group after methylation (Hirst and Jones, *J.*, 1939, 454). Only two possibilities, therefore, for the monomethyl derivative remained. It could be either 2- or 3-methyl *l*-arabinose. The latter was thought to be the sugar present in the hydrolysis products of the methylated araban since the amide from the syrupy hydrolysis product gave a positive Weerman test, indicating the presence of an α-hydroxy-amide. It has now been ascertained that this positive test was due to the presence of a small quantity of *l*-arabonamide in the crude syrupy amide, a trace of *l*-arabinose being present in the monomethyl arabinose fraction owing to the difficulty encountered in separating

these two high boiling fractions. In order to obtain further insight into the constitution of the monomethyl arabinose the two sugars, 2- and 3-methyl *l*-arabinose were synthesised and crystalline derivatives of them were prepared (Jones, Kent, and Stacey, in the press; Hirst, Jones, and Williams, in the press). Crystalline derivatives have now been obtained from the monomethyl fraction of the hydrolysis products from methylated araban, and by comparison of these with the synthetic material it has been established beyond doubt that the monomethyl fraction consists almost exclusively of 2-methyl *l*-arabinose (see experimental section). The isolation of the crystalline 2-methyl *l*-arabinose phenylhydrazone, 2-methyl 3 : 4-monoacetone *l*-arabinose, and 2-*methyl* l-*arabonamide* derivatives from the monomethyl fraction was aided by the previous preparation of synthetic crystalline derivatives and by the fact that larger quantities of methylated araban of higher purity were available. This was rendered possible by the observation that araban, which was the major component of the pectin, was methylated much more rapidly than galactan and pectic acid and that the latter can be converted into soluble acid products on heating with 30% sodium hydroxide in the presence of air without destruction of the araban.

With the larger quantities of methylated araban available, it was possible to carry out a rigorous fractionation of the methylated product and thus to obtain a homogeneous product which showed $[\alpha]_D^{20°}$ — 180° in methyl alcohol. It was demonstrated, from observation of the refractive indices and methoxyl values of the fractions obtained on distillation of the products of methanolysis of the methylated araban, that trimethyl, dimethyl, and monomethyl arabinoses are present in equimolecular proportions. The trace of unmethylated arabinose which is also present appears to arise either through incomplete methylation of the polysaccharide or by demethylation of the arabinose fractions during methanolysis.

From these observations the general type of structure present in the araban becomes apparent. The polysaccharide contains only the three residues $A1\ldots.$, $\ldots 5A1\ldots.$, and $\cdots{}^{3}_{5}A1\ldots$ present in equimolecular proportions, A representing an arabofuranose unit linked through the positions indicated. A branched chain structure with terminal arabofuranose residues is clearly present, but the present data do not enable us to differentiate between a main chain of arabofuranose residues composed solely of $\cdot\cdot{}^{5}_{3}A1\ldots$ residues and one comprising both this residue and $\ldots 5A1\ldots.$ From rotational data the *l*-arabofuranoside links have the α-configuration, and the general lines of the structure are illustrated in (I) which represents one



(I)

of the formulæ consonant with the experimental observations, but it is obvious that certain simple variations of this formula are also in agreement with the available experimental evidence. The problem of distinguishing between these requires the development of novel methods of attack, and experimental work is now being undertaken with this object in view. The branched chain of this polymer, which is composed only of *l*-arabofuranose residues, proves that the araban cannot be formed in the plant directly, as a polymer, by simple processes of oxidation and decarboxylation from either the galactan or the pectic acid associated with pectin. The origin and mechanism of the formation of araban remains therefore to be determined.

Experimental.

The seeds (14 kg.) were defatted with benzene and the protein was removed in the usual manner. The residual material was extracted with aqueous potassium hydroxide and crude araban isolated using the conditions described by Hirst and Jones (*loc. cit.*). A portion (50 g.) of the isolated polysaccharides (100 g.) was methylated with sodium hydroxide and methyl sulphate. After two methylations crude methylated araban was isolated by the addition of acetone followed by filtration of the solution to remove insoluble sodium salts and polysaccharide material. After the insoluble methylated material had been separated the aqueous solution was acidified and extracted with chloroform. Concentration of the extract gave some methylated pectic acid (4 g.), $[\alpha]_D^{18°}$ + 114° (*c*, 0·57 in methyl alcohol) (Found: OMe,

38%). The filtered acetone solution on evaporation gave a pale yellow sticky solid which was further methylated by use of Purdie's reagents. The polysaccharide (35 g.) was fractionated from chloroform (100 c.c.) by the gradual addition of light petroleum (b. p. 40—60°), giving:

Fraction A (0·9 g.), mainly inorganic material.
Fraction B (6·2 g.), $[\alpha]_D^{25°}$ — 144° (*c*, 1·1 in methyl alcohol) (Found: OMe, 38·7%).
Fraction C (15 g.), $[\alpha]_D^{25°}$ — 176° (*c*, 1·3 in methyl alcohol) (Found: OMe, 38·3%).
Fraction D (8·1 g.), $[\alpha]_D^{25°}$ — 180° (*c*, 0·7 in methyl alcohol) (Found: OMe, 38·0%).
Fraction E (4·0 g.), $[\alpha]_D^{25°}$ — 179° (*c*, 0·9 in methyl alcohol) (Found: OMe, 38·0%).

All these fractions were pale yellow sticky solids. The residue (1·0 g.) was discarded.

Trial Hydrolysis.—Fraction D (7·9 g.) was dissolved in methyl alcohol (75 c.c.)–water (25 c.c.) containing oxalic acid dihydrate (0·1 g.) and boiled under reflux in an attempt to bring about a graded hydrolysis of the polysaccharide (see Hirst and Young, *J.*, 1939, 1480). The optical rotation (— 184°) remained constant and no hydrolysis occurred during 20 hours under these conditions even when the oxalic acid concentration was raised to 0·5 g./100 c.c. Accordingly, oxalic acid was removed by neutralisation with calcium carbonate and the unchanged polysaccharide submitted to hydrolysis with boiling methyl alcohol (100 c.c.) containing hydrogen chloride (2 g.) for 30 hours. Change of optical rotation could not be observed owing to darkening of the solution. The cooled solution was neutralised by cautious addition of ethereal diazomethane and the solvents were removed at 60°. The residual syrup (9·4 g.) was then fractionated by continuous extraction from aqueous solution (Z) with light petroleum (b. p. 40—60°) giving an extract—*Fraction* 1 (2·89 g.), $n_D^{19°}$ 1·4360—which was distilled yielding *Fraction* 1*a* (2·54 g.), b. p. 130°/12 mm., $n_D^{18°}$ 1·4352 (Found: OMe, 60·0%), and a still residue (0·28 g.). The aqueous solution (Z, above) was then extracted continuously with ether and the extracts concentrated at 40° to a syrup—*Fraction* 2 (3·68 g.)—which was added to the still residue (0·28 g. above) and the whole fractionally distilled giving *Fraction* 2*a* (1·3 g.), b. p. 120°/0·2 mm., $n_D^{22°}$ 1·4452 (Found: OMe, 52·3%); *Fraction* 2*b* (1·87 g.), b. p. 125°/0·01 mm., $n_D^{21°}$ 1·4487 (Found: OMe, 47·8. Calc. for $C_8H_{16}O_5$: OMe, 48·4%); still residue (S, 0·62 g.). The aqueous solution (Z) after extraction with light petroleum and ether was evaporated in a vacuum to a syrup which was combined with the still residue (S, 0·62 g.) and the mixture (2·8 g.) distilled under reduced pressure giving *Fraction* 3*a* (0·25 g.), b. p. 125°/0·01 mm., $n_D^{22°}$ 1·4582 (Found: OMe, 43·7%); *Fraction* 3*b* (1·06 g.), b. p. 125°/0·01 mm., $n_D^{23°}$ 1·4662 (Found: OMe, 42·2%); *Fraction* 3*c* (0·68 g.), b. p. 125°/0·01 mm., $n_D^{23°}$ 1·4750 (Found: OMe, 24·8%), and a still residue (0·76 g.) (Found: OMe, 25·1%).

Fraction 1a on hydrolysis gave 2 : 3 : 5-trimethyl *l*-arabofuranose in quantitative yield, $[\alpha]_D^{20°}$ — 38° (in water), identified by conversion into the crystalline lactone, m. p. 29°, of 2 : 3 : 5-trimethyl *l*-arabonolactone and into 2 : 3 : 5-trimethyl *l*-arabonamide, m. p. 139°. Fraction 2a was a mixture of the methyl glycosides of 2 : 3 : 5-trimethyl *l*-arabofuranose and 2 : 3-dimethyl *l*-arabinose since it was separated into 2 : 3 : 5-trimethyl methyl-*l*-arabinoside (0·90 g.), identified as crystalline 2 : 3 : 5-trimethyl *l*-arabonolactone, m. p. 29°—prepared in the usual manner—and 2 : 3-dimethyl methyl-*l*-arabinoside (0·35 g.), $n_D^{22°}$ 1·4454, on fractional extraction from aqueous solution with light petroleum (b. p. 40—60°). This last fraction was combined with Fraction 2b and the whole (2·1 g.) hydrolysed with N-hydrochloric acid at 100°; $[\alpha]_D^{20°}$ — 35° ⟶ $[\alpha]_D^{20°}$ + 92° (constant value). The resultant syrup (1·9 g.) ($[\alpha]_D^{18°}$ + 104°, *c*, 1·1 in water) (Found: OMe, 34·4. Calc. for $C_7H_{14}O_5$: OMe, 34·6%), isolated in the usual manner, was mainly if not entirely 2 : 3-dimethyl *l*-arabinose since it gave, in good yield, the corresponding 2 : 3-dimethyl anilino-*l*-arabinose, m. p. and mixed m. p. 139°. On refluxing it with alcoholic aniline, no other derivative of arabinose could be detected.

Fractions 3a and 3b were combined (1·80 g.) and separated by fractional extraction from water with ether into 2 : 3-dimethyl methyl-*l*-arabinoside (0·8 g.), identified, after hydrolysis to 2 : 3-dimethyl *l*-arabinose with N-hydrochloric acid, as 2 : 3-dimethyl anilino-*l*-arabinose, m. p. and mixed m. p. 139°. The more water-soluble fraction (1·0 g.) was 2-monomethyl methyl-*l*-arabinoside which was combined with Fraction 3c and the whole (1·65 g.) hydrolysed with boiling N-sulphuric acid (25 c.c.); $[\alpha]_D^{20°}$ + 81° (constant value) ⟶ + 94° (constant value after 6 hours). The residual syrup (1·3 g.) did not crystallise (Found: OMe, 19·4. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). A sample, on refluxing with alcoholic phenylhydrazine, gave 2-methyl *l*-arabinose phenylhydrazone, m. p. and mixed m. p. 115° (see below). On shaking a sample of the syrup with acetone and anhydrous copper sulphate, 2-methyl monoacetone *l*-arabinose was formed in quantitative yield, m. p. and mixed m. p. 117° (Found: C, 52·7; H, 7·8; OMe, 15·2. Calc. for $C_9H_{16}O_5$: C, 52·9; H, 7·8; OMe, 15·2%).

A portion (0·66 g.) of the still residue was hydrolysed with hot N-sulphuric acid (18 c.c.). The syrup (0·56 g.), $[\alpha]_D$ + 92° (Found: OMe, 17·4%), isolated in the usual manner was almost entirely 2-methyl *l*-arabinose since it gave the corresponding crystalline phenylhydrazone, m. p. and mixed m. p. 115°, on refluxing with an alcoholic solution of phenylhydrazine. Some *l*-arabinose was also present since the syrup gave, in small yield with an alcoholic solution of benzoylhydrazine, a precipitate of *l*-arabinose benzoylhydrazone, m. p. 184°.

Large Scale Hydrolysis of Methylated Araban.—Fraction C (14·46 g.) was hydrolysed by boiling with methanolic hydrogen chloride (100 c.c.; 1%) for 12 hours. Changes in optical rotation were not observable owing to darkening of the solution. The cooled solution was neutralised with a slight excess of diazomethane in ether and the solvents were removed as quickly as possible at 70°. The syrupy residue (17·1 g.) was then dissolved in water (50 c.c.) and extracted continuously for 24 hours in an all-glass apparatus with light petroleum (sulphur-free, b. p. 35—37°). After removal of the solvent at 40° there remained a syrup (7·05 g., $n_D^{22°}$ 1·4388). The aqueous solution was then extracted continuously for a further 24 hours with ether. Concentration of the extracts gave a syrup (4·75 g.). The residual aqueous solution on removal of water gave a syrup (5·2 g.) which was extracted with chloroform, giving a syrup (5·0 g.) soluble in chloroform and leaving crystalline β-methyl-*l*-arabopyranoside (0·2 g.), m. p. 164—168° not depressed on admixture with an authentic specimen.

Fractional Distillation of the Syrups.—The light-petroleum-soluble syrup (7·05 g., $n_D^{22°}$ 1·4388) was

distilled at 20 mm., giving: *Fraction* 4 (4·94 g.), b. p. 145° (bath temp.), $n_D^{21°}$ 1·4359 (Found: OMe, 59·2. Calc. for $C_9H_{18}O_5$: OMe, 60·2%); *Fraction* 5 (1·46 g.), b. p. 155°, $n_D^{21°}$ 1·4432 (Found: OMe, 54·0. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). The still residue (0·69 g.) was added to the ethereal extract (4·75 g.) and the whole distilled at 0·01 mm. giving *Fraction* 6 (2·34 g.), b. p. 110° (bath temp.), $n_D^{22°}$ 1·4515 (Found: OMe, 48·4. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). The syrup soluble in chloroform (5 g., see above) was added at this stage and the distillation continued. *Fraction* 7 (2·55 g.), b. p. 140° (bath temp.), $n_D^{24°}$ 1·4565 (Found: OMe, 48·1. Calc. for $C_8H_{16}O_5$: OMe, 48·4%); *Fraction* 8 (2·11 g.), b. p. 155° (bath temp.), $n_D^{24°}$ 1·4672 (Found: OMe, 40·3. Calc. for $C_7H_{14}O_5$: OMe, 34·8%); *Fraction* 9 (1·06 g.), b. p. 160° (bath temp.), $n_D^{20°}$ 1·4715 (Found: OMe, 34·9. Calc. for $C_7H_{14}O_5$: OMe, 34·8%); *Fraction* 10 (0·65 g.), b. p. 190° (bath temp.), $n_D^{20°}$ 1·4745 (Found: OMe, 32·1. Calc. for $C_7H_{14}O_5$: OMe, 34·8%). The still residue (1·20 g.) (Found: OMe, 30·5%) was methylated with Purdie's reagents (see below).

Examination of the Fractions.—A portion of Fraction 4 (4·84 g.) was dissolved in N-sulphuric acid (25 c.c.) and hydrolysed at 90° for 3½ hours; $[\alpha]_D^{20°}$ — 86° ⟶ — 30° (constant value). The sugar (4·5 g.) was isolated by continuous extraction of the solution with chloroform (Found: OMe, 48·0. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). The sugar was converted into 2 : 3 : 5-trimethyl *l*-arabonolactone by the following general method. The sugar (4·5 g.) was dissolved in N-sodium hydroxide (150 c.c.), and iodine (12 g.) added. After 12 hours, excess of iodine was removed with sulphur dioxide and the solution then acidified with sulphuric acid and extracted continuously with chloroform. Concentration of the chloroform extract gave a syrup (4·3 g.), $n_D^{20°}$ 1·4448, which crystallised on nucleation with 2 : 3 : 5-trimethyl *l*-arabonolactone, m. p. and mixed m. p. with an authentic specimen, 28°. This fraction therefore consists entirely of 2 : 3 : 5-trimethyl methyl-*l*-arabinoside.

Fraction 5 (1·45 g.) was dissolved in N-sulphuric acid (25 c.c.) and hydrolysed on the steam-bath; $[\alpha]_D^{20°}$ — 81° ⟶ $[\alpha]_D^{20°}$ + 30° (final value). The free sugars (1·35 g.) isolated in the usual manner (Found: OMe, 41·8%) were oxidised with bromine (2 c.c.) in water (5 c.c.) for 12 hours. The lactones—isolated by chloroform extraction of the solution after removal of excess of bromine—were distilled in a vacuum giving impure 2 : 3 : 5-trimethyl *l*-arabonolactone (0·7 g.), m. p. 20°, and impure 2 : 3-dimethyl *l*-arabofuranolactone, b. p. 130° (bath temp.)/0·4 mm., $n_D^{21°}$ 1·4578. The lactones gave, with alcoholic ammonia, the corresponding crystalline amides, *viz.*, 2 : 3 : 5-trimethyl *l*-arabonamide, m. p. 138°, and 2 : 3-dimethyl-*l*-arabonamide, m. p. 161°. It is inferred that this fraction consists of 2 : 3 : 5-trimethyl and 2 : 3-dimethyl methyl-*l*-arabinoside in approximately equal proportion.

Fraction 6 (2·22 g.) was hydrolysed by boiling with N-sulphuric acid (20 c.c.) for 3 hours; $[\alpha]_D^{20°}$ — 51° ⟶ + 101° (constant value). The resultant 2 : 3-dimethyl *l*-arabinose (2·0 g.) was isolated by exhaustive chloroform extraction of the solution after neutralisation with N-sodium hydroxide. Since this fraction showed an inversion of sign the material was 2 : 3-dimethyl methyl-*l*-arabinoside mainly in the furanose form.

Fraction 7 (2·42 g.) was dissolved in N-sulphuric acid and hydrolysed by heating the solution to 90°; $[\alpha]_D^{20°}$ + 56° ⟶ + 102° (constant value). The syrupy sugar was isolated from the neutralised solution by exhaustive chloroform extraction (yield, 2·2 g.). This fraction was 2 : 3-dimethyl methyl-*l*-arabinoside mainly in the pyranose form.

The sugars from Fractions 6 and 7 were combined (4·2 g.), $[\alpha]_D^{20°}$ + 104° (*c*, 1·3 in water) (Found: OMe, 34·6. Calc. for $C_7H_{14}O_5$: OMe, 34·8%), and oxidised by dissolving in water (10 c.c.) containing bromine (5 c.c.). The solution became hot and was left for 12 hours. Bromine was then removed, first by aeration, and then by passage of sulphur dioxide. The solution was then extracted exhaustively with chloroform and the resultant 2 : 3-dimethyl *l*-arabofuranolactone (4·1 g.) purified by distillation in a vacuum; b. p. 140° (bath temp.)/0·5 mm., $n_D^{24°}$ 1·4575. With alcoholic ammonia the lactone gave 2 : 3-dimethyl *l*-arabonamide, m. p. 162°, in quantitative yield.

Fraction 8 was a mixture of 2 : 3-dimethyl methyl-*l*-arabinoside and 2-methyl methyl-*l*-arabinoside. Partial separation of the components was achieved by the following method. The glycosides (2·0 g.) were dissolved in acetone (25 c.c.) containing hydrogen chloride (1 g.) (see Hirst and Jones, *J.*, 1939, 456). After 20 hours the solution was poured into an aqueous solution of sodium hydrogen carbonate and the neutral solution extracted with chloroform. The extracts were dried (K_2CO_3), filtered, and concentrated to a syrup (1·74 g.) which was distilled under reduced pressure giving a first fraction, b. p. 106° (bath temp.)/0·5 mm. (0·6 g.), $n_D^{20°}$ 1·4500 (Found: OMe, 30·0. Calc. for 2-methyl monoacetone methyl-*l*-arabinoside: OMe, 28·4%), and a second fraction, b. p. 120°/0·5 mm. (0·8 g.), $n_D^{20°}$ 1·4610 (Found: OMe, 43·0. Calc. for 2 : 3-dimethyl methyl-*l*-arabinoside: OMe, 48·4%). The still residue was mainly 2-methyl methyl-*l*-arabinoside (Found: OMe, 36·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%). The impure 2-methyl monoacetone methyl-*l*-arabinoside (0·5 g.) was hydrolysed with boiling N-sulphuric acid, $[\alpha]_D^{20°}$ + 100° (final value), and the sugar (0·3 g.) isolated in the usual manner. It was identified, after boiling with alcoholic phenylhydrazine, as 2-methyl *l*-arabinose phenylhydrazone, m. p. and mixed m. p. 115°. This same derivative was isolated after boiling the free sugar, obtained from the hydrolysis of the still residue with hot N-sulphuric acid, with alcoholic phenylhydrazine. The second fraction (above) on hydrolysis with boiling N-sulphuric acid (20 c.c.) gave 2 : 3-dimethyl *l*-arabinose which was identified as its anilide, obtained by boiling an alcoholic solution of the sugar with aniline, m. p. 138° not depressed on admixture with an authentic specimen.

Fractions 9 and 10 consisted of 2-methyl methyl-*l*-arabinoside. These fractions were combined and the syrup (1·65 g.) hydrolysed with boiling N-sulphuric acid (20 c.c.); $[\alpha]_D^{20°}$ + 104° (final value; initial value not observable). The free sugar (1·5 g.) was isolated after neutralisation of the solution with barium carbonate followed by filtration and concentration under reduced pressure (Found: OMe, 18·7. Calc. for $C_6H_{12}O_5$: OMe, 18·9%).

A portion of the syrup (0·1 g.) on heating with alcoholic phenylhydrazine gave 2-methyl *l*-arabinose phenylhydrazone (0·1 g.), m. p. 115° not depressed on admixture with an authentic specimen. The syrup (0·4 g.) was oxidised with bromine (1 c.c.) in water (5 c.c.) at 30° for 12 hours. Bromine was removed by aeration and the 2-methyl *l*-arabonolactone isolated by exhaustive extraction of the solution

with chloroform. The lactone (0·35 g.) did not crystallise, but with an alcoholic solution of ammonia it gave 2-*methyl* l-*arabonamide* (0·3 g.), $[\alpha]_D$ + 51° (*c*, 1·1 in water), m. p. 130° depressed to 124° on admixture with 3-methyl *l*-arabonamide, m. p. 131° (Found : C, 40·1; H, 7·4; N, 7·8; OMe, 17·2. $C_6H_{13}O_5N$ requires C, 40·2; H, 7·3; N, 7·8; OMe, 17·3%). 2-Methyl *d*-arabonamide has $[\alpha]_D$ − 53° (in water), m. p. 131° (Schmidt and Simon, *J. pr. Chem.*, 1942, **152**, 199).

To prove the absence of any quantity of 3-methyl *l*-arabinose, the following procedure was adopted. The syrupy sugar (1·0 g.) was boiled with 3% methyl-alcoholic hydrogen chloride for 24 hours to ensure a maximum conversion into the pyranoside derivative. The solution was neutralised with silver carbonate and filtered, and the residual non-reducing syrup (0·92 g.), $[\alpha]_D^{20°}$ + 143° (*c*, 0·9 in water), was dissolved in water and oxidised with excess of sodium periodate solution (30 c.c.; 0·3M) for 24 hours. The aqueous solution was then extracted, first with ether, which is known to extract monomethyl methyl-*l*-arabinoside very slowly indeed, and then with chloroform. Concentration of the ethereal extract gave a mobile reducing syrup (0·7 g.) from which no identifiable product could be isolated. The chloroform extract on concentration gave a sticky brown solid (0·2 g.), which on hydrolysis with N-sulphuric acid was completely decomposed with the formation of resinous products. No 3-methyl *l*-arabinose, which would not have been oxidised with sodium periodate, could be detected, nor could any derivative of 3-methyl *l*-arabinose be isolated. It is concluded that any appreciable quantity of 3-methyl *l*-arabinose is absent from the products of hydrolysis of methylated araban.

The still residue (1·2 g.) was methylated with silver oxide and methyl iodide (twice) and the syrupy sugar distilled in a vacuum giving a mobile syrup (0·9 g.), $n_D^{20°}$ 1·4480 (Found : OMe, 59·1%), which on hydrolysis with boiling N-sulphuric acid gave 2 : 3 : 4-trimethyl *l*-arabinose, $n_D^{20°}$ 1·4540, $[\alpha]_D^{20°}$ + 112° (*c*, 1·1 in water) (Found : OMe, 46·0%).

On oxidation with bromine water the syrup (0·4 g.) gave the corresponding δ-lactone, isolated as the crystalline amide, m. p. 95° (Found : OMe, 44·2. Calc. for $C_8H_{17}O_5N$: OMe, 44·9%).

From an examination of the various fractions, it may be calculated from the values of refractive index and methoxyl of each fraction that the sugars 2 : 3 : 5-trimethyl *l*-arabinose, 2 : 3-dimethyl *l*-arabinose, and 2-methyl *l*-arabinose are present in a ratio approximating very closely to 1 : 1 : 1.

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