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Studies on Arabogalactans

II. Fractionation of the Arabogalactan from *Larix occidentalis* Nutt. A Methylation Study of one of the Components

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The arabogalactan from Western Larch (*Larix occidentalis* Nutt.) heartwood has been separated into two components by fractional precipitation of their borate complexes with cetyl-trimethylammoniumhydroxide. These differ in electrophoretic mobility in borate buffer and in sedimentation velocity but have about the same composition and optical rotation. Methylation and hydrolysis of the component with the higher molecular weight afforded 2-*O*-methyl-D-galactose, 2,4-di-*O*-methyl-D-galactose, 2,6-di-*O*-methyl-D-galactose, 2,3,4-tri-*O*-methyl-D-galatose, 2,4,6-tri-*O*-methyl-D-galactose, 2,3,4,6-tetra-*O*-methyl-D-galactose, 2,5-di-*O*-methyl-L-arabinose, 2,3,4-tri-*O*-methyl-L-arabinose and 2,3,5-tri-*O*-methyl-L-arabinose, which were separated, characterised and estimated quantitatively.

FRACTIONATION OF THE ARABOGALACTAN

The homogeneity of the arabogalactans from the *Larix* genus has long been under discussion. In ultracentrifuge studies of a larchwood arabogalactan (species not stated) Mosimann and Svedberg [1] found two components with approximate molecular weights of 16 000 and 100 000. In Western Larch arabogalactan Lystad-Borgin [2] found only one component in the heartwood but two in the sapwood. The molecular weight of these components seemed to be of the same order as those calculated by Mosimann and Svedberg, the heartwood component having the higher molecular weight. Fractional precipitation of the polysaccharide, either directly or after methylation or acetylation has given opposite results (*cf.* Ref.[3]). In a recent publication Aspinall *et al.*[4] concluded that the arabogalactan from European Larch, *L. decidua* Miller, was homogeneous, since no proof of heterogeneity could be found. The heterogeneity of the arabogalactan from Western Larch (*L. occidentalis* Nutt.) heartwood which was left undecided in a previous communication [5] has now been investigated. Electrophoresis of the polysaccharide on glass fibre sheets using borate buffer showed the presence of two components (A and B), which gave two distinct spots on development of the electrophoretograms.

Cetyl-trimethylammonium bromide and similar quaternary ammonium salts have been used succesfully by Scott [6] and others for the fractionation of acidic polysaccharides. Barker *et al.*[7] recently showed that the method could also be applied to neutral polysaccharides capable of forming borate complexes. When this method was used for the fractionation of larch arabogalactan, only part of one component (A), the more mobile on electrophoresis, could be precipitated. The incompleteness of the fractionation was probably caused by to high an ionic strength in the solution. The method was therefore modified by using the corresponding base, cetyl-trimethylammoniumhydroxide, together with boric acid and this gave almost complete precipitation of the polysaccharide. The addition of a small amount of sodium hydroxide had a favourable coagulating effect. The fractionations were made in 4—5 steps at pH 7—8; usually only one of the fractions contained both components. As the mixed fractions were easily refractionated by the same procedure, the original material could be separated completely into the two components.

The proportion of A to B was about 2:1. A, $[\alpha]_D^{20}$ +7° (in water), contained 19 % (molar) arabinose and B, $[\alpha]_D^{20}$ +10°, 21 % arabinose. Sedimentation analysis, made by courtesy of Prof. S. Claesson, Dept. of Physical Chemistry, Uppsala University, gave sedimentation constants 4.3 and 1.4, resp., for A and B in good agreement with the values previously reported [1,2]; the components appeared in the approximate proportion of 2:1. The molecular weights of A and B are therefore of the same magnitude, 100 000 and 16 000, as those calculated for the two components in the sample studied by Mosimann and Svedberg.

A METHYLATION STUDY OF ARABOGALACTAN A

Arabogalactan A was methylated first with methyl sulphate and sodium hydroxide and then with methyl iodide and silver oxide in dimethyl formamide. The latter procedure, devised by Kuhn *et al.*[8] for carbohydrates of low molecular weight, proved to be valuable for polysaccharides also. It was, however, necessary to modify the method of isolation of the methylated product in order to improve the yield. After four methylations in dimethyl formamide the product had a methoxyl content of 44.4 % (theoretical value 44.7 %). The usual methods of estimating the completeness of the methylation of a polysaccharide are not unambiguous; those using methoxyl analyses and infrared spectrophotometry are both open to criticism. Besides the methoxyl analysis a good criterion of the completeness of methylation in the present case was also found in the absence of even traces of unmethylated monomers in the hydrolysate of the methylated polysaccharide.

The hydrolysate from the methylated polysaccharide was fractionated by chromatography on carbon and cellulose columns and on thick filter papers. Carbon columns, in some cases combined with filter paper chromatography, proved most satisfactory for the separation of ethers with at least one free alcoholic hydroxyl; separation on cellulose columns gave better results for highly methylated ethers. The results from the fractionation of the hydrolysate are summarised in Table 1. The ethers were either obtained crystalline or characterised as crystalline derivatives.

Table 1. Galactose and arabinose methyl ethers isolated from the hydrolysate of 0.96 g of methylated arabogalactan A.

Methyl Ethers	mmoles	molar %
2-Methylgalactose	0.14	3.7
2,4-Dimethylgalactose	1.42	37.5
2,6-Dimethylgalactose	0.11	2.9
2,3,4-Trimethylgalactose	0.52	13.7
2,4,6-Trimethylgalactose	0.16	4.2
2,3,4,6-Tetramethylgalactose 2,3,5-Trimethylarabinose	1.22	32.2
2,5-Dimethylarabinose	0.12	3.2
2,3,4-Trimethylarabinose	0.10	2.6

As is often found in this type of investigation, the number of end groups, represented by the tetramethyl galactose and trimethyl arabinose, was smaller than that required by the number of branching points as determined by the amount of mono- and dimethyl galactoses. Incomplete methylation, possibly demethylation during the acid hydrolysis and losses due to the volatility of the fully methylated monomers will all contribute to this discrepancy. A recent publication of Gardiner and Percival [9] has emphasised the last possibility. In the present investigation it was found that about 5 % of a sample of tetramethyl galactose was lost on concentration of an aqueous solution under the conditions used in the quantitative estimation of the ether. Further, if 2,3,4-tri-*O*-methyl-L-arabinose and 2,5-di-*O*-methyl-L-arabinose are derived entirely from 3-*O*-β-L-arabopyranosyl-L-arabofuranose units [10,5], the difference in the amounts of these ethers gives a measure of the deficiences of the methods used.

It is difficult to decide whether the occurrence of 2-*O*-methyl-D-galactose and 2,6-di-*O*-methyl-D-galactose has any structural significance as an indication of the presence of 1,4-linkages. As the hydroxyl group at $C_{(4)}$ in a galactose residue is axial, it is presumably less reactive in the methylation (*cf.* Ref.[11]). The results of a partial methylation of 6-trityl-β-methyl-D-galactoside also indicated that this hydroxyl group is less reactive [12]; in this case, however, steric interaction from the trityl group might be of some importance. If 2-*O*-methyl-D-galactose and 2,6-di-*O*-methyl-D-galactose were the results of demethylation of 2,4-di-*O*-methyl-D-galactose and 2,4,6-tri-*O*-methyl-D-galactose or incomplete methylation of residues, corresponding to these ethers, it would be expected that these pairs of methyl ethers would be formed in about same proportion. However, the proportions actually found are 1.3:1 and 8.8:1. Therefore, and in view of the virtual absence of other monomethyl and dimethyl ethers of galactose, this strongly supports the structural significance of 2-*O*-methyl-D-galactose and 2,6-di-*O*-methyl-D-galactose.

2,3,5-Tri-*O*-methyl-L-arabinose and 2,3,4,6-tetra-*O*-methyl-D-galactose did not separate on the carbon column; separation of the corresponding fraction on thick filter paper afforded the arabinose ether but this was impure and in insufficient quantity for proper characterisation. A larger amount of methylated polysaccharide was therefore subjected to a mild hydrolysis and the low-molecular part of the hydrolysate was hydrolysed further and then frac-

tionated on a cellulose column. The first fraction afforded 4.5 % (molar) of pure 2,3,5-tri-*O*-methyl-L-arabinose; a further quantity of this ether appeared in the following fraction which contained mainly 2,3,4,6-tetra-*O*-methyl-D-galactose. As the hydrolysis of the arabinose residues was not taken to completion, this figure does not represent the total amount of terminal arabofuranosidic units.

It was therefore not possible to make a quantitative estimation of the relative amounts of 2,3,5-tri-*O*-methyl-L-arabinose and 2,3,4,6-tetra-*O*-methyl-D-galactose. In view of the proportion of arabinose to 3-*O*-β-L-arabopyranosyl-L-arabinose (5.9:2) formed on partial hydrolysis [5], it seems reasonable to assume that about 2/3 of the arabinose is present as terminal arabofuranose units and 1/3 as 3-*O*-β-L-arabopyranosyl-L-arabofuranose. Therefore, taking the values for 2,5-di-*O*-methyl-L-arabinose and 2,3,4-tri-*O*-methyl-L-arabinose also into consideration, the arabinose content of the original polysaccharide could be estimated as 18—19 % (molar), in good agreement with the value 18.7 %, found by quantitative paper chromatography.

The relatively low percentage of galactose trimethyl ethers indicates that the arabogalactan A has a more branched structure than previously investigated polysaccharides of similar type; the isolation of 2-*O*-methyl-D-galactose suggests a small number of doubly branched units. The galactose residues are substituted in the 3- and 6-positions to about the same extent with linkages of the β-pyranoside type. A small number of 1,4-linkages seems to be present. There is 18—19 % (molar) of arabinose, about one third of which is combined as 3-*O*-β-L-arabopyranosyl-L-arabofuranose and the remainder as terminal L-arabofuranose residues.

The results previously reported of a partial hydrolysis of the arabogalactan strongly indicated the presence of galactofuranosidic residues in the polysaccharide. An additional, chromatographic investigation of A and B separately revealed no fundamental differences between the two components in this respect. However, no furanoside methyl ethers of galactose were found in the present investigation. This does not necessarily imply that galactofuranosidic residues are not present in arabogalactan A, since the experimental methods used were inadequate for the isolation of the corresponding ethers in the presence of large amounts of other ethers. This problem therefore requires further examination.

A comparison of the results of the present investigation with those of previous studies of related polysaccharides is of interest but must await the structure investigation of arabogalactan B.

EXPERIMENTAL

Melting points are corrected. All evaporations were carried out under reduced pressure.

Chromatography. Papers: Whatman No. 1 and 3 MM and Schleicher and Schüll 602 hP. Solvent: Butanol, ethanol, water, 10:3:5. Developer: Anisidine hydrochloride.

Paper electrophoresis. Paper: Schleicher and Schüll Glass Fibre Paper. Developer: α-Naphthol/sulphuric acid in butanol.

Preparation of larch arabogalactan. The polysaccharide was prepared mainly as described in part I[5]. It was purified further by filtering through ion exchange columns

(Amberlite IR-120 and IR-4B) and treatment with Floridin before being concentrated. It was obtained as a light-coloured powder on precipitation from ethanol. The arabinose content was 16.3 %, determined according to Saeman *et al* [13].

Electrophoresis of arabogalactan. The electrophoretograms (14 × 50 cm) were run in borate buffer at pH 10 for 30—45 min at 2 000 V and 30—50 mA. To allow for electroosmosis, which is very pronounced on glass fibre papers, the non-complexforming ω-hydroxymethylfurfural was used as reference substance. On development the electrophoretograms gave two distinct spots, the denser one (A) moving about 30 % faster than the other (B).

Sedimentation analysis of arabogalactan. Sedimentation analysis revealed two components with sedimentation constants (S_{20}) of 4.3 (A) and 1.4 (B) in the proportion 2:1. Determination on the pure components, prepared as described below, gave the same sedimentation constants (4.3 and 1.4). Both components showed considerable polymolecularity but were found to be essentially free of the other component.

Fractionation of arabogalactan. In a typical experiment the polysaccharide (40 g = 0.25 mole anhydrosugar) was dissolved in water (1 000 ml) and 0.6 M boric acid (415 ml). Cetyltrimethylammonium hydroxide (CTA-OH) was prepared by filtering an aqueous solution of the corresponding bromide through a hydroxyl-saturated column of Dowex 2 ion exchange resin. A portion of this solution (0.095 N) was added to the polysaccharide solution which became cloudy but formed no precipitate until a small amount of sodium hydroxide was added. The sticky precipitate thus obtained was collected on a glass filter and washed thoroughly with water. A further portion of CTA-OH and of sodium hydroxide was added to the filtrate and the fresh precipitate collected. The residual solution was deionised, concentrated and the remaining boric acid was removed by evaporation with methanol, giving a small quantity of polysaccharide which was isolated in the usual manner by precipitation with ethanol. To regenerate the polysaccharides, the precipitates obtained above were dissolved in the miniumum amount of 6 % acetic acid and poured into ethanol; the different fractions were obtained as white powders after filtering and drying. The results of the fractionation are summarised in Table 2. The mixed fraction was dissolved in water (500 ml) and 0.6 M boric acid (120 ml); 0.095 N CTA-OH (52 ml) and 0.5 N sodium hydroxide (5 ml) were added, the precipitate formed was collected and the polysaccharide was isolated as desribed above. 8.0 g of pure arabogalactan A was obtained; the residual solution afforded 3.2 g of mixed material. The arabogalactan fractions thus obtained were electrophoretically pure.

Table 2. Fractionation of 40 g of larch arabogalactan.

0.095 N CTA-OH added (ml)	0.50 N NaOH added (ml)	Weight of fraction (g)	Components
105	5	14.6	A
105	10	11.6	A + B
105	10	5.9	B
52	20	1.5	B
Residue	—	2.1	B

Methylation of arabogalactan A. The polysaccharide (5.70 g) was dissolved in 22.5 % sodium hydroxide (60 ml) under a nitrogen atmosphere. Methyl sulphate (30 ml) was added in small portions over 6 h while the solution was stirred vigorously and cooled with ice water. After a further 2 h the reaction mixture was neutralised with dilute sulphuric acid, dialysed over night against running tap water and then de-ionised by filtering through columns of Amberlite resins IR-120 and IR-4B. After concentration to dryness, the polysaccharide was dissolved in chloroform and precipitated in light petroleum. Yield 6.07 g (93 %); OCH_3 = 26.7 %.

The premethylated polysaccharide (6.05 g) was dissolved in 60 ml of freshly distilled dimethyl formamide (DMFA) and dry methyl iodide (25 ml). The solution was stirred vigorously and cooled while silver oxide (20 g) was added in portions over one hour. After

a reaction time of 20 h the polysaccharide was isolated as described by Kuhn *et al.*[9] for the isolation of fully methylated low-molecular weight carbohydrates. Precipitation in light petroleum gave 5.39 g (82 %), OCH_3 = 41.7 %.

This product (5.29 g) was methylated 20 h with methyl iodide (8 ml) and silver oxide (6 g) in DMFA (50 ml). The reaction mixture was centrifuged and the solid material was thoroughly washed with DMFA and chloroform. The combined centrifugates were concentrated almost to dryness and benzene (150 ml) was added. The precipitated silver salts were filtered off. The precipitate was treated with a small volume of hot DMFA, poured into benzene and filtered. The combined filtrates were concentrated and, if necessary, filtered again. The product was isolated either as a glass or by precipitation in light petroleum as a yellowish powder. This methylation was repeated twice. The final methylation gave 4.15 g of methylated arabogalactan A; OCH_3 = 44.4 % (theoretical value 44.7 %), $[\alpha]_D^{20}$ −37° (*c*, 1.0 in ethanol). The average yield for each methylation was thus 92 %. No trace was found of unmethylated arabinose and galactose on hydrolysis of the methylated polysaccharide.

Separation of methyl ethers from hydrolysed, methylated arabogalactan A. Methylated arabogalactan A (0.96 g) was heated in formic acid (60 ml) at 100° for 6 h. The formyl esters obtained on concentration were hydrolysed by heating in hydrochloric acid (100 ml, 0.5 N) at 100° for 10 h. After neutralising by filtration through an ion exchange column (IR-4B) and concentration of the solution, the hydrolysate was added to the top of a carbon-Celite column (3.5 × 43 cm) and eluted, using the gradient elution technique[14], with 5 l 6—24 % ethanol + 2.5 l 24—50 % ethanol + 1 l 60 % acetone. Table 3 shows how the fractions (25 ml each) were combined; the amount of sugar present was estimated by hypoiodite oxidation[15] and weighing.

A similar preparative separation was made using 2.0 g of methylated polysaccharide and gave crystalline 2-*O*-methyl-D-galactose, 2,4-di-*O*-methyl-D-galactose and 2,6-di-*O*-methyl-D-galactose; the other ethers, except 2,3,5-tri-*O*-methyl-L-arabinose were obtained in quantities sufficient for the preparation of derivatives. Except for the identifications, this separation will not be described in detail.

Fractions 146—159 contained about 50 % each of 2,3,4-trimethylgalactose and 2,5-dimethylarabinose, as estimated by paper chromatograms. Fractions 95—106, 107—119

Table 3. Fractionation of hydrolysed, methylated arabogalactan A.

Fract. No.	Amount of red. sugars as determined by hypoiodite oxid. mmoles	hypoiodite oxid. mg	weighing mg	Principal sugars present
27— 37	0.137	27	29	2-methylgalactose
53— 94	1.385	288	295	2,4-dimethylgalactose
95—106	0.094	19	20	2,4-dimethylgalactose 2,6-dimethylgalactose
107—119	0.540	117 *	118	2,3,4-trimethylgalactose 2,3,4-trimethylarabinose
120—145	0.195	40 *	41	2,3,4-trimethylgalactose 2,5-dimethylarabinose
146—159	0.046	10	14	2,3,4-trimethylgalactose 2,5-dimethylarabinose
160—192	0.162	36	39	2,4,6-trimethylgalactose
217—285	1.102	253 **	256	2,3,4,6-tetramethylgalactose 2,3,5-trimethylarabinose
60 % acetone eluate	0.120	28 **	30	2,3,4,6-tetramethylgalactose 2,3,5-trimethylarabinose

* Calculated from values given below. ** Calc. as 2,3,4,6-tetramethylgalactose.

Table 4.

Fract. No	Sugars	Equiv. in ml. 0.01 N $Na_2S_2O_3$	%	mmoles
95—106	2,4-dimethylgalactose	0.81	20	0.019
(0.094 mmoles)	2,6-dimethylgalactose	3.18	80	0.075
107—119	2,4-dimethylgalactose	0.09	1.9	0.010
(0.540 mmoles)	2,6-dimethylgalactose	0.19	4.0	0.022
	2,3,4-trimethylgalactose	3.60	75.8	0.409
	2,3,4-trimethylarabinose	0.87	18.3	0.099
120—145	2,4,-dimethylgalactose	0.11	4.0	0.008
(0.195 mmoles)	2,6-dimethylgalactose	0.14	5.0	0.010
	2,3,4-trimethylgalactose	1.19	42.7	0.083
	2,5-dimethylarabinose	1.35	48.3	0.094

and 120—145 were analysed in the following way. A suitable quantity (7—9 mg) of each fraction was separated on thick filter paper (Schleicher and Schüll 602 hP). The substances were located in the usual way, eluted from the corresponding strips with water and a quantitative estimation was made by hypoiodite oxidation. The following results were obtained (Table 4). Combination of these analytical data gives the values shown in Table 1.

Partial hydrolysis of methylated arabogalactan A. Exhaustively methylated polysaccharide (6.3 g) was boiled for six days in 0.02 N sulphuric acid containing 30 % ethanol. The solution was neutralised with barium carbonate and concentrated to dryness; the hydrolysate was dissolved in benzene, precipitated in light petroleum and filtered. The solid material was re-precipitated twice and the combined filtrates concentrated to a lightcoloured syrup (1.74 g), which was further hydrolysed in 0.5 N hydrochloric acid to split the methylated oligosaccharides present.

*Isolation of 2,3,5-tri-O-methyl-*L*-arabinose.* This product was added to the top of a cellulose column and eluted with butanol saturated with water. The top fraction afforded 282 mg of 2,3,5-tri-*O*-methyl-L-arabinose (4.5 % calculated on the original material). The following fraction contained mainly 2,3,4,6-tetra-*O*-methyl-D-galactose and a lesser quantity of the arabinose ether.

Characterisation of the methyl ethers

*2-O-Methyl-*D*-galactose.* The ether was crystallised from ethanol, m.p. and mixed m.p. 150—152°. On chromatography and electrophoresis, the ether was indistinguishable from an authentic sample of 2-*O*-methyl-D-galactose.

*2,4-Di-O-methyl-*D*-galactose.* The ether was crystallised from moist ethyl acetate, m.p. 103°, sintering at 80°; m.p. of the corresponding aniline derivative 216—219°. The ether was converted to the osazone, m.p. 146—149°, undepressed on admixture with an authentic sample of 4-*O*-methyl-D-galactosazone. On electrophoresis in borate buffer the ether, as expected, was immobile.

*2,6-Di-O-methyl-*D*-galactose.* The ether was recrystallised from ethyl acetate, m.p. 120—122°, undepressed on admixture with a synthetic sample. On electrophoresis in borate buffer, it moved somewhat more slowly than 2-*O*-methyl-D-galactose but decidedly faster than 4-*O*-methyl-D-galactose, as would be expected for a galactose derivative, capable of forming a complex only between $C_{(3)}$ and $C_{(4)}$ [12].

*2,3,4-Tri-O-methyl-*D*-galactose.* The ether was converted to the aniline derivative, m.p. 170—171°, undepressed on admixture with an authentic specimen.

*2,4,6-Tri-O-methyl-*D*-galactose.* The ether was converted to the aniline derivative, m.p. 179—180°. For further characterisation, a portion of the ether was reduced with

sodium borohydride. The trimethylgalactitol thus obtained consumed no periodate. This is in agreement with a 2,4,6-tri-*O*-methyl-D-galactose structure for the original ether which is the only pyranosidic trimethylgalactose of which the corresponding galactitol derivative is not oxidised by periodate.

2,3,4,6-Tetra-O-methyl-D-galactose. The ether was converted to the aniline derivative, m.p. 198—200°, undepressed on admixture with an authentic sample.

2,5-Di-O-methyl-L-arabinose. This was somewhat faster on paper chromatogram than 2,3,4-tri-*O*-methyl-L-arabinose and yielded arabinose only on demethylation. It was converted to the corresponding amide, m.p. 132—133°, in good agreement with values previously reported [16].

2,3,4-Tri-O-methyl-L-arabinose. The ether was converted to the corresponding phenylhydrazide, m.p. 157—158°, undepressed on admixture with an authentic specimen.

2,3,5-Tri-O-methyl-L-arabinose. The ether was faster on paper chromatogram than 2,3,4,6-tetra-*O*-methyl-D-galactose and gave arabinose on demethylation. It was converted to the corresponding arabonamide, m.p. 139—140°, in good agreement with values previously reported [16].

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