$f_8$fars, and the mixed ligands f_nAsP. Indeed, because of this, it is difficult to assign this band with any certainty. In the monosubstituted series $(CH_3)_2AsC{=}CF(CF_2)_{n/2}$ the strong $\nu(C{=}C)$ changes very little with ring size, it being 1662, 1661, and 1664 cm^{-1} for $n = 4$, 6, and 8 respectively. In the C—F stretching region, the pattern and position of absorption for the di-substituted compounds ($f_n$fars, f_nAsP, $f_n$fos) with a given ring size is very similar. The ν(C—F) are $1308 \pm 4, \sim 1227, 1154 \pm 5, 1106 \pm 6$ cm^{-1} for $n = 4$; $\sim 1331, 1236 \pm 3, 1187 \pm 3, 1136 \pm 5, 1092 \pm 2, 1000 \pm 7$ cm^{-1} for $n = 6$; and $1344 \pm 1, 1213 \pm 5, 1193 \pm 5, 1177 \pm 2, 1162 \pm 4, 1109 \pm 7, 1038 \pm 3, 980 \pm 8$ cm^{-1} for $n = 8$.

All the derivatives which possess a $(CH_3)_2As$ group show a doublet in the region 565–585 cm^{-1} which is associated with As—CH_3 stretching vibrations and which is fairly insensitive to the nature of the other substituents on the arsenic(III) atom. The values for other compounds not listed in Table 4 are 568, 581, $f_4$fars; 565, 580, $(CH_3)_2AsC{=}CF(CF_2)_2CF_2$; 562, 584 cm^{-1} $(CH_3)_2AsC{=}CFCF_2CF_2$.

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Synthesis of 6-*O*-(4-*O*-Methyl-β-D-glucopyranosyl)-D-galactose

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6-*O*-(4-*O*-Methyl-β-D-glucopyranosyl)-D-galactose has been synthesized by a Koenigs–Knorr reaction. The disaccharide is most readily characterized in the form of the crystalline glycosyl alditol peracetate.

Le 6-*O*-(4-*O*-methyl-β-D-glucopyranosyl)-D-galactose a été synthétisé selon la methode de Koenigs–Knorr. Le disaccharide est plus facilement identifié sous forme du glycosyl alditol peracétate.

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In studying the structure of acidic polysaccharides it is often more convenient to carry out fragmentation after the uronic acid function has been reduced, a transformation which is readily achieved with diborane (1) or complex hydrides (2, 3). Similarly, an aldobiouronic acid may more readily be characterized as the derived neutral disaccharide (*e.g.* 4, 5). The aldobiouronic acid 6-*O*-(4-*O*-methyl-β-D-glucopyranosyluronic acid)-D-galactose is found in many plant gums (6–8) and it is thus of interest to prepare 6-*O*-(4-*O*-methyl-β-D-glucopyranosyl)-D-galactose. This note reports the synthesis and characterization of this disaccharide and of the related disaccharide alditol.

4-*O*-Methyl-D-glucose was prepared by Hakomori methylation (9) of 2,3:5,6-di-*O*-isopropylidene-D-glucose dimethyl acetal which was obtained via the diethyl thioacetal and purified through the crystalline *p*-nitrobenzoate (10). This sugar was identified as the osazone (10, 11) and the β-D-tetraacetate (12), both crystalline.

2,3,6-Tri-*O*-acetyl-4-*O*-methyl-α-D-glucopyranosyl bromide was condensed with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (13) in chloroform using freshly prepared silver oxide (14). The reaction product was deacetylated with sodium methoxide to give 6-*O*-(4-*O*-methyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-D-galactopyranose as a crystalline material in 62% yield. Preliminary experiments showed that the ketal groups could be removed with minimal hydrolysis of the glycosidic linkage by 0.05 *N* sulfuric acid on a steam bath for 40 min. Hydrolysis in this way gave 6-*O*-(4-*O*-methyl-β-D-glucopyranosyl)-D-galactose as a

syrup in 90% yield. Examination by paper chromatography showed a very small amount (<5%) of monosaccharide and pure disaccharide was obtained as a syrup by passage through Dowex 50W X2 (Li^+) (15). The disaccharide had $[\alpha]_D \sim 0°$ in water consistent with the assignment of a β-D-linkage. According to Hudson's rules (16) the calculated values for $[\alpha]_D$ are approximately +93 and −6° for α-D- and β-D-(1→6) links.

The disaccharide consumed 4.9–5.0 mol of periodate and successive borohydride reduction and total hydrolysis gave ethylene glycol and 2-*O*-methyl-D-erythritol identified by g.l.c. of their trimethylsilyl derivatives (17). Methylation (Hakomori) of the disaccharide followed by methanolysis and g.l.c. indicated the presence of 2,3,4,6-tetra-*O*-methyl-D-glucose together with 2,3,4- and 2,3,5-tri-*O*-methyl-D-galactose (18). It is of interest to note that the Hakomori method of methylation, like the Kuhn reagents (19), gives a high proportion of the furanose isomer. The peak areas for the 2,3,4- and 2,3,5-isomers were in the approximate ratio of 3:2. No satisfactory crystalline derivatives were obtained from the disaccharide which was most conveniently characterized as the glycosyl alditol acetate, m.p. 104–106°. The n.m.r. spectrum of the free glycosyl alditol in deuterium oxide showed $J_{1,2}$ 7.5 Hz (τ 5.3) consistent with a β-D-linkage (20).

Experimental

Thin-layer chromatography was carried out using solvent systems A and B on silica gel. Plates were developed by spraying with 50% aqueous sulfuric acid and heating to about 150° for 3–5 min. Paper chromatograms using solvent systems C and D were developed using silver nitrate in acetone for reducing sugars (21) and sodium periodate – benzidine for non-reducing compounds (22). Solvent A, ethyl ether – toluene (2:1); B, butanone–water azeotrope; C, ethyl acetate – pyridine–water (4:1:1); D, ethyl acetate – acetic acid–formic acid – water (18:3:1:4). Gas–liquid chromatography was carried out on a F and M 720 instrument using columns: (*a*) 8 ft × 1/4 in. 20% SF 96 on 80–100 mesh Diatoport S, (*b*) 4 ft × 1/4 in. 5% butanediol succinate on 80–100 mesh Diatoport S, and (*c*) 2 ft × 1/4 in. 20% SE 30 (F and M Division, Hewlett–Packard, Arondale, Pennsylvania). The n.m.r. spectra were recorded on a Varian HA-100 instrument using tetramethylsilane as internal standard except as noted. Optical rotations were measured at 23 ± 1° on a Rudolph polarimeter model 219 and later on a Perkin-Elmer model 141 polarimeter. Melting points are uncorrected. Solvents were removed *in vacuo* at a bath temperature not exceeding 40°.

4-O-Methyl-D-glucose

2,3:5,6-Di-*O*-isopropylidene-D-glucose dimethyl acetal (10 g) (10) was dissolved in dry methyl sulfoxide (100 ml), a solution of methyl sulfinyl anion (0.6 *M*, 120 ml) was added and the solution left 45 min at room temperature (23). Excess methyl iodide was then added while keeping the temperature below 25°. Thin-layer chromatography in solvent A showed the reaction to be complete in 30 min. Petroleum ether (65–110°, 400 ml) and water (200 ml) were added and the water layer extracted with petroleum ether (8 × 100 ml). The combined solvent extracts were washed, dried, and concentrated to give a syrup (9.6 g) which was heated for 4 h at 60° with sulfuric acid (0.05 *N*, 100 ml). Neutralization ($BaCO_3$) and concentration gave crude 4-*O*-methyl-D-glucose (5.7 g), [α] +49° (*c*, 2 in water). A pure sample obtained by sodium methoxide deacetylation of the tetraacetate had [α] +60.0° (*c*, 2.8 in water), lit. (11) $[\alpha]_D$ +61.1° (*c*, 2 in water); $R_{glucose}$ 2.65 (solvent C). Phenylosazone m.p. 158–160°, (lit. (10, 11) m.p. 158–160°).

Crude 4-*O*-methyl-D-glucose (4.5 g) was acetylated with acetic anhydride (32 ml) and anhydrous sodium acetate (2.25 g) to give the tetraacetate, (3.58 g), m.p. 98–100°. 1,2,3,6-Tetra-*O*-acetyl-4-*O*-methyl-β-D-glucopyranose (**1**) was recrystallized from cyclohexane and had m.p. 102–103°, $[\alpha]_D$ −8.1° (*c*, 2.3 in chloroform), (lit. (12) m.p. 98–99°, $[\alpha]_D$ −7° (*c*, 2 in chloroform)), the n.m.r. data ($CDCl_3$) $J_{1,2}$ 8.0 Hz (τ 4.40) (24).

Anal. Calcd. for $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. Found: C, 49.62; H, 6.05.

2,3,6-Tri-O-acetyl-4-O-methyl-α-D-glucopyranosyl Bromide (**2**)

Tetraacetate (**1**) (1.6 g) was dissolved in cold hydrogen bromide in glacial acetic acid (32%, 28 ml) and the solution allowed to stand at room temperature for 45 min. Chloroform (50 ml) was added and the solution was shaken with water (50 ml). The aqueous layer was extracted with chloroform (3 × 25 ml) and the combined extracts were washed with saturated sodium hydrogen carbonate (2 × 50 ml) and cold water (2 × 25 ml). Evaporation of the dried chloroform gave (2) as a syrup (1.8 g), [α] +190° (*c*, 4.2 in chloroform).

6-O-(4-O-Methyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-D-galactopyranose (3)

1,2:3,4-Di-*O*-isopropylidene-D-galactopyranose (**4**) (600 mg, 2.5 mmol, distilled syrup), freshly prepared silver oxide (2.0 g), and Drierite (2.0 g, finely powdered, preheated to 200° *in vacuo*) were stirred for 1 h in absolute chloroform (15 ml) at room temperature. A solution of the bromide **2** (1.5 g, 3.7 mmol) in absolute chloroform (8 ml) was then added over 2 h with continuous stirring. Thin-layer chromatography (solvent A) showed R_f values as follows: **2**, 0.54; product, 0.44; **4**, 0.33; and a compound, assumed to be a degradation product of **2**, at 0.28. Thin-layer chromatography further showed that the reaction was complete 30 min after the final addition. The mixture was filtered, the solid was washed with chloroform, and the filtrate and washings evaporated to a syrup which was reacted directly with sodium methoxide (0.1 *N*, 30 ml). After 30 min sodium ion was removed with Amberlite IR 120 resin and the methanol evaporated to give a solid product, m.p. 168–170° (680 mg, 62%). Recrystallization from ethanol (4 ml/g)

gave pure **3** m.p. 174–175°, $[\alpha]_D$ −60.5° (*c*, 0.8 in methanol), R_f (t.l.c., solvent B) 0.50.

Anal. Calcd. for $C_{19}H_{32}O_{11}$: C, 51.88; H, 7.35; OMe, 6.93. Found: C, 52.25; H, 7.39; OMe, 7.11.

*6-O-(4-O-Methyl-*D*-glucopyranosyl)-*D*-galactose*

Compound **3** (600 mg) was heated on a steam bath for 40 min in sulfuric acid (0.05 *N*, 30 ml). Passage through Duolite A-4 resin and concentration gave the disaccharide as a syrup (486 mg), $[\alpha]_D$ +4° (*c*, 1 in water); $R_{glucose}$ 0.34 (solvent C); 0.26 (solvent D) on paper chromatography. These conditions of hydrolysis were chosen when 0.5 *N* sulfuric acid and Amberlite IR-120 resin were found to give glycosidic cleavage and 0.01 *N* sulfuric acid required heating for 90 min. Removal of isopropylidene groups was followed by t.l.c. in solvent B and paper chromatography (solvents C and D) was used to check on glycosidic cleavage. Purification of 100 mg of disaccharide on Dowex 50W X2 (Li^+) gave a recovery of 94 mg, $[\alpha]_D$ ~0° (*c*, 1 in water). Solid products were obtained by reaction with phenylhydrazine, aniline (m.p. 145–147°) and *p*-nitrobenzoyl chloride (m.p. 153–156°) none of which gave satisfactory analyses.

The g.l.c. of the per(trimethylsilyl) disaccharide (column c at 260°) gave one peak (~15%) at 7.3 min and two unresolved peaks at 10.7 min (per(trimethylsilyl)sucrose 5.5 min).

Anal. Calcd. for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.74. Found (after drying over P_2O_5 at 68° for 3 days): C, 43.63; H, 7.09.

Reaction of the pure disaccharide (10.40, 10.50 mg) in duplicate oxidations with sodium metaperiodate (0.015 *M*, 20 ml) at room temperature in the dark showed a rapid uptake of 4 mol with the consumption of periodate becoming constant (4.9, 5.0 mol) in 18 h (25). Iodate and excess periodate were removed by addition of barium acetate and sodium borohydride was added. The polyalcohol, obtained by deionization, distillation with methanol and concentration, was hydrolyzed (1.0 *N* H_2SO_4, 5 ml, 100°, 4h) and the neutralized ($BaCO_3$) hydrolyzate converted to trimethylsilyl derivatives. Injection in hexane, onto column *a* programmed from 120 to 195° at 2°/min, gave peaks identical to authentic standards of the per(trimethylsilyl) derivatives of ethylene glycol (5.3 min) and 2-*O*-methyl-D-erythritol (27.2 min) (4, 26).

Pure disaccharide (28 mg) in dry methyl sulfoxide (2.0 ml) was methylated using methyl sulfinyl anion (1.5 *M*, 1.0 ml) and methyl iodide (6.0 ml). Methanolysis and examination of the methyl glycosides on column *b* programmed from 130 to 190° at 2°/min showed peaks corresponding to methyl 2,3,4,6-tetra-*O*-methyl-D-glucosides (5.1, 7.7 min), methyl 2,3,5-tri-*O*-methyl-D-galactofuranosides (15.9 min), and methyl 2,3,4-tri-*O*-methyl-D-galactopyranosides (21.3 min).

*6-O-(4-O-Methyl-β-*D*-glucopyranosyl)-*D*-galactitol (5)*
*[1-O-(4-O-Methyl-β-*D*-glucopyranosyl)-*L*-galactitol]*

Disaccharide (180 mg) was reduced with sodium borohydride (360 mg) in water (18 ml) for 4 h. Passage through cation exchange resin, concentration and distillation with methanol gave **5** ($R_{glucose}$ 0.34, solvent C; 0.33 solvent D) which was acetylated with acetic anhydride (10 ml) and anhydrous sodium acetate (500 mg). The peracetate of **5** was obtained as a syrup which crystallized on seeding with crystals obtained by g.l.c. Crude yield 346 mg, m.p. 95–100°. Two recrystallizations from ethanol (20 ml/g) gave 6-*O*-(4-*O*-methyl-β-D-glucopyranosyl)-D-galactitol octaacetate m.p. 104–106°, $[\alpha]_D$ −31.3° (*c*, 2.2 in chloroform), R_f 0.35 solvent A). Retention time on column *c* at 275° 8.0 min (sucrose octaacetate 5.1 min). The n.m.r. spectrum of the acetate in $CDCl_3$ did not show clearly the signal for the anomeric proton but the free alditol **5** in D_2O showed $J_{1,2}$ 7.5 Hz (τ 5.53, Me_4Si external) (20).

Anal. Calcd. for $C_{29}H_{42}O_{19}$: C, 50.12; H, 6.10. Found: C, 50.09; H, 6.07.

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