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SOME REACTIONS OF FURANOID GLYCALS

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ABSTRACT

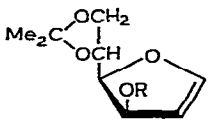
The reaction of 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**1**) with *m*-chloroperbenzoic acid in ethanol gives 2,3-unsaturated ethyl glycosides together with saturated ethyl glycosides formed by trans-ring opening of 1,2-epoxide intermediates. Similar results are obtained on peroxidation of 1,4-anhydro-2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl)-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**2**). Products resulting from osmylation of **1** and **2** and cleavage of the osmate esters are also described. 2-Deoxy derivatives are prepared from **1** and **2** by methoxymercuration–demercuration and also by reduction of 2-bromo-2-deoxy derivatives obtained by ethoxybromination.

DISCUSSION

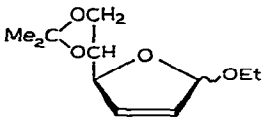
Pyranoid glycals (1,5-anhydro-2-deoxyald-1-enitols) are useful in synthetic carbohydrate chemistry because of their unusual reactivity and their ease of transformation and isomerisation[1]. In contrast, because general methods for their preparation have not been available, the chemistry of furanoid glycals (1,4-anhydro-2-deoxyald-1-enitols) has received little attention, and only their catalytic hydrogenation and some rearrangement reactions have been investigated[2–4].

Recently, efficient methods have been described[5–6] for the preparation of furanoid glycals by reaction of furanosyl halides, protected with base-stable groups, with alkali metals in inert solvents, and we now report on the results of some addition reactions to the double bonds of the furanoid glycals **1** and **2**.

Oxidation of 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**1**) with *m*-chloroperbenzoic acid in absolute ethanol gave mainly an anomeric mixture of rearranged products, the hex-2-enofuranosides **3** (26%), and also two ethyl furanosides **7** (7%) and **8** (15%). The β-D-*gluco* configuration for **7** and the α-D-*manno* configuration for **8** were established from n.m.r. data: both **7** and **8** showed small $J_{1,2}$ values (≤2 Hz), indicating[7] a trans relationship between H-1 and H-2. These assignments were confirmed by the n.m.r. spectra of the acetates **9** and **10** which were, respectively, similar to those of other β-D-glucofuranoses[8] and to that of the 2,3,5,6-tetra-acetate **4** prepared from the known methyl α-D-mannofuranoside[9].



1 R = H
2 R = 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl



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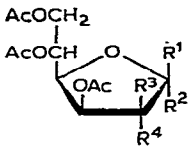
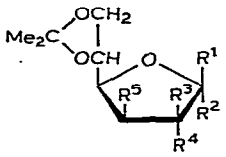


4 $R^1 = R^4 = H$, $R^2 = OMe$, $R^3 = OAc$
5 $R^1 = R^4 = OAc$, $R^2 = R^3 = H$
6 $R^1 = R^3 = H$, $R^2 = R^4 = OAc$



M = 2,3:5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl

	R^1	R^2	R^3	R^4	R^5		R^1	R^2	R^3	R^4	R^5
7	OEt	H	H	OH	OH	**22**	OMe	H	H	H	OM
8	H	OEt	OH	H	OH	**23**	OEt	H	H	Br	OH
9	OEt	H	H	OAc	OAc	**24**	H	OEt	H	Br	OH
10	H	OEt	OAc	H	OAc	**25**	OEt	H	H	Br	OAc
11	OEt	H	H	OH	OM	**26**	H	OEt	H	Br	OAc
12	OEt	H	H	OAc	OM	**27**	OEt	H	mixture H,Br		OM
13	*m*-Cl-CO_2Ph	H	H	OAc	OM	**28**	mixture H,OH		H	Br	OM
14	H	*m*-Cl-CO_2Ph	H	OAc	OM	**29**	OAc	H	H	Br	OM
15	OAc	H	H	OAc	OAc	**30**	H	OAc	H	Br	OM
16	H	OAc	H	OAc	OAc	**31**	OEt	H	H	H	OH
17	H	OAc	H	OAc	OM	**32**	OEt	H	H	H	OAc
18	OAc	H	H	OAc	OM	**33**	OEt	H	H	H	OM
19	mixture H,OAc		OAc	H	OM	**34**	H	OEt	H	H	OAc
20	OMe	H	H	H	OAc	**35**	OAc	H	H	H	OM
21	H	OMe	H	H	OAc	**36**	H	OAc	H	H	OM

1,4-Anhydro-2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl)-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol (**2**) reacted much more cleanly with *m*-chloroperbenzoic acid in ethanol than the glycal **1**. Clearly, steric hindrance by the bulky group at C-3 gave rise to preferential attack from the α-side by the oxidant, and rearrangement reactions were also inhibited; the β-D-glucoside **11** (62%), yielding **12** on acetylation, was the major product, while the minor products included an anomeric mixture of D-glucofuranosyl *m*-chlorobenzoates (~3%) that yielded two separable acetates **13** and **14**. A mixture of two unidentified ethyl glycosides (~2%) was also isolated.

The multiplicity and coupling constants of the H-1 and H-2 signals of the

acetate **12** and the *m*-chlorobenzoate **13** establish[7,8] their β-D-*gluco* configuration, as well as that of **11** from which **12** was obtained.

The fact that **14** was more dextrorotatory than **13**, as would be expected[10] for the α anomer of an anomeric pair of D-glycosides, and the preponderance of D-*gluco* products isolated from the hydroxylation reaction, suggested that **14** is an α-D-*gluco* rather than a β-D-*manno* derivative; it is clear from the n.m.r. spectrum that H-1 and H-2 of **14** are cis.

The reaction of the glycal **1** with osmium tetraoxide in pyridine, followed by cleavage of the osmate ester, acetylation of the products, and chromatography, yielded only the β-D- and α-D-glucofuranoses, **15** (30%) and **16** (17%), respectively, indicating that attack by the oxidant took place mainly from the α-face. The preparation of a mixture of **15** and **16** has been described[11] previously, but chemical and physical properties of the individual compounds were not reported.

Compound **15** has an n.m.r. spectrum consistent with a β-D-glucofuranose structure and was converted by mild hydrolysis with acid and acetylation into the known[8] penta-*O*-acetyl-β-D-glucofuranose (**5**). Similar treatment of the anomer **16** afforded the α-D analogue **6**. In compliance with Hudson's isorotation rules[10], **6** is more dextrorotatory than **5**. Also, the $J_{1,2}$ value for **16** shows that H-1 and H-2 are cis, and base-catalysed deacetylation yielded D-glucose.

As expected, the stereospecificity of the osmylation reaction of the glycal **2** was controlled, to a large extent, by the bulky C-3 substituent, and, after cleavage of the osmate ester and acetylation, chromatography afforded the anomeric *gluco*-furanoses **17** and **18** and a mixture of the *manno*-furanoses **19** in a ~7:1 ratio of *gluco*:*manno* derivatives.

The assignment of the configurations of **17** and **18** and of the mixture **19** was based on n.m.r. and optical rotatory properties, and was confirmed by degradative studies. Thus, catalytic deacetylation with base, followed by acid hydrolysis, gave a mixture of D-glucose and D-mannose from **17** and **18**, but only D-mannose from the mixture **19**.

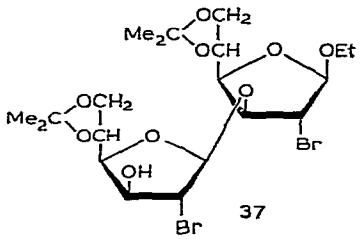
The conversion of the glycals **1** and **2** into 2-deoxyglycosides was achieved by both the methoxymercuration–demercuration[12] and ethoxybromination–debromination[13] methods.

Treatment of **1** with mercury(II) acetate in dry methanol, followed by demercuration with sodium borohydride, gave a crude mixture that yielded **20** and **21** on acetylation and chromatography. The configurations of **20** and **21** followed[10] from their optical rotatory properties, with the β-D anomer **20** being more levorotatory than the α-D anomer **21**.

Methoxymercuration–demercuration of **2** gave only one product **22**, probably having the anomeric methoxyl group in the β configuration, as the n.m.r. parameters are comparable with those of **20**.

Ethoxybromination of **1** with *N*-bromosuccinimide (NBS) in acetonitrile–ethanol gave mainly the ethyl β-D-glucoside **23** (28%), with the α-D-glucoside **24** (3%), the disaccharide **37**, and the known[5] furan **38** (6%) as minor products. A

consideration of n.m.r. coupling criteria[7-8], similar to those discussed previously, established that H-1 and H-2 of **23** and its 3-acetate **25** are trans, whereas H-1 and H-2 of **24** and its 3-acetate are cis. Also, debromination experiments, followed by comparison[10] of specific rotations (see later), proved that **25** has a β- and **26** an α-anomeric substituent; **23–26** are therefore D-*gluco* derivatives.



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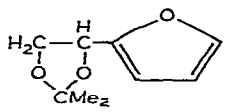

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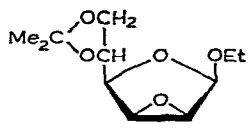

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The formation of the disaccharide **37** can be rationalized by assuming that, in a side-reaction, the intermediate cyclic bromonium-ion[13] formed from the reaction of NBS with **1** is attacked at the anomeric centre by HO-3 of **23**, rather than by ethanol.

The n.m.r. spectrum of the disaccharide **37** displayed a singlet and a narrow doublet ($J \sim 1$ Hz) for the two anomeric protons, showing[10] that H-1 and H-2 of both furanosyl rings are trans. As it was established that the products of ethoxybromination **23** and **24** have the D-*gluco* configuration, it is reasonable to assume that both furanosyl rings of **37** also have the D-*gluco* configuration.

Ethoxybromination of **2** gave a mixture that was partially fractionated, to give a mixture of ethyl 2-bromo-2-deoxy-furanosides **27** (19%) and an anomeric mixture of a 2-bromo-2-deoxy-furanose **28**.

Clearly, the anomeric mixture **28** was formed by attack of water, present as an impurity, on the bromonium-ion intermediate formed during the ethoxybromination reaction. Acetylation of **28** gave the separable, anomeric acetates **29** and **30**.

Reductive debromination of **23** with lithium aluminium hydride in tetrahydrofuran gave the 2,3-anhydrofuranoside **39** (56%) and the 2-deoxy-furanose **31** (17%) which was acetylated to give **32**.

Similar reduction of **27** gave only an ethyl 2-deoxy-furanoside **33**, with $[\alpha]_D$ −21°. In comparison, **35** and **36** (see later), which are analogues of **33** in which the ethoxyl group has been replaced by a β- and an α-acetyl group, respectively, have $[\alpha]_D$ −22° and +32°. These data indicate that **33** is an ethyl β-D-furanoside, and it follows that **27** is a mixture of ethyl 2-bromo-2-deoxy-β-D-manno- and -gluco-furanosides.

High yields of the debrominated products **32** and **34** were obtained by reducing[13] the respective 2-bromo-2-deoxy compounds **25** and **26** with tributylstannane in the presence of the radical initiator α,α′-azobis(isobutyronitrile) in benzene. Compound **34** was more dextrorotatory than its anomer **32**, and is therefore[10] the α-D anomer. This finding established that **23** and **25** are β-D-*gluco* derivatives and that **24** and **26** are α-D-*gluco* derivatives (see earlier discussion of the n.m.r. spectra of **23** and **24**).

Tributylstannane reduction of the acetates **29** and **30** gave **35** and **36**, respectively. Again, it is clear from the n.m.r. spectra that H-1 and H-2 are trans in **29**, and cis in **30**. The specific rotations indicate that **35** is the 2-deoxy-β-furanose and that **36** is the 2-deoxy-α-furanose, and it follows that **29** and **30** are β- and α-D-*gluco* derivatives, respectively.

EXPERIMENTAL

General methods. — All solvent extracts were dried (silica gel), filtered, and concentrated *in vacuo* below 50°. T.l.c. and column chromatography were performed on silica gel (Merck GF_{254}; 100 g per g of residue for column separations). Unless stated otherwise, i.r. spectra were measured for thin films and optical rotations for solutions in chloroform with a Perkin–Elmer 237 spectrophotometer and 241 automatic polarimeter (*c* 1.0 ±0.3), respectively. Mass spectra (70 eV) were determined with an A.E.I. MS-9 spectrometer by direct insertion. N.m.r. spectra were recorded on a Varian HA-100 or XL-100 instrument, for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. For syrups, microanalytical figures are given only for distilled products. Otherwise, accurate mass measurements were made on the detectable ions of highest mass.

*Ethyl 2,3-dideoxy-5,6-*O*-isopropylidene-α- and β-*D-erythro-*hex-2-enofuranoside* (**3**), *ethyl 5,6-*O*-isopropylidene-α-*D-*mannofuranoside* (**8**), *and ethyl 5,6-*O*-isopropylidene-β-*D-*glucofuranoside* (**7**). — Glycal **1** (0.35 g, 1.9 mmol) in absolute ethanol (5 ml) was treated with *m*-chloroperbenzoic acid (0.32 g, 1.9 mmol) at 0° for 25 min. The solution was evaporated, and a solution of the residue in ethyl acetate was washed with saturated, aqueous sodium hydrogen carbonate. Evaporation of the organic phase gave an oil that was chromatographed [ethyl acetate–hexane (3:2)] to give the glycosides **3** as an oil (83 mg, 26%), $[\alpha]_D^{20}$ −13°. Mass spectrum: *m/e* 199 (M^+ — Me) and 169 (M^+ — OEt). N.m.r. data: τ ~3.76 (m, 2 H, 2 H-2), 4.2 (m, 4 H, 2 H-1,3), ~5.3 (m, 2 H, 2 H-4), 5.8–6.7 (10 H, 2 H-5,6a,6b, 2 CH_2Me), 8.61 and 8.69 (2 s, 12 H, 4 Me), and 8.78 and 8.82 (2 t, 6 H, 2 CH_2Me).

Anal. Calc. for $C_{10}H_{15}O_4$ (M^+ — 15): 199.097. Found: 199.097.

Further elution gave furanoside **8** as an oil (32 mg, 7%), $[\alpha]_D^{20}$ +31°, ν_{max} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 233 (M^+ — Me). N.m.r. data: τ 5.06 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), ~5.6 (m, 2 H, sharpens on addition of D_2O, H-2,3), 5.7–6.18 (m, 4 H, H-4,5,6a,6b), 6.3 (m, 2 H, CH_2Me), 6.6 (br, 2 H, disappears on addition of D_2O, 2 OH), 8.58 and 8.65 (2 s, 6 H, 2 Me), and 8.82 (t, 3 H, *J* 7 Hz, CH_2Me).

Anal. Calc. for $C_{10}H_{17}O_6$ (M^+ — 15): 233.151. Found: 233.151.

The diacetate (**10**) of **8** was an oil, $[\alpha]_D^{20}$ +73°, ν_{max} 1755 cm^{-1} (CO). Mass spectrum: *m/e* 317 (M^+ — Me). N.m.r. data: τ 4.42 (m, 1 H, H-3), 4.80 (dd, 1 H, $J_{2,3}$ 5, $J_{2,1}$ 3 Hz, H-2), 4.99 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.7–6.1 (m, 4 H, H-4,5,6a,6b), 6.4 (m, 2 H, OCH_2Me), 7.95 and 7.97 (2 s, 6 H, 2 OAc), 8.64 and 8.7 (2 s, 6 H, 2 Me), and 8.83 (t, 3 H, *J* 7 Hz, OCH_2Me).

Anal. Calc. for $C_{15}H_{24}O_8$: C, 54.2; H, 7.3. Found: C, 54.4, H, 7.2.

Further elution gave furanoside **7** as an oil (70 mg, 15%), $[\alpha]_D^{20}$ −37°, ν_{max} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 233 (M^+ — Me). N.m.r. data: τ 5.09 (s, 1 H, H-1), 5.6–6.1 (m, 6 H, H-2,3,4,5,6a,6b), 6.3 (m, 2 H, CH_2Me), 6.5 (br s, 1 H, disappears on addition of D_2O, OH), 6.90 (br d, 1 H, disappears on addition of D_2O, OH), 8.58 and 8.64 (2 s, 6 H, 2 Me), and 8.82 (t, 3 H, *J* 7 Hz, CH_2Me).

Anal. Calc. for $C_{11}H_{20}O_6$: C, 53.2; H, 8.1. Found: C, 53.3; H, 7.9.

The diacetate (**9**) of **7** was an oil, $[\alpha]_D^{20}$ −11°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 317 (M^+ — Me). N.m.r. data: τ 4.66 (br d, 1 H, $J_{3,4}$ 4 Hz, H-3), 4.94 (br s, 1 H, H-2), 5.08 (s, 1 H, H-1), 5.6–6.02 (m, 4 H, H-4,5,6a,6b), 6.4 (m, 2 H, CH_2Me), 7.92 and 7.93 (2 s, 6 H, 2 OAc), 8.62 and 8.69 (2 s, 6 H, 2 Me), and 8.8 (t, 3 H, *J* 7 Hz, CH_2Me).

Anal. Calc. for $C_{15}H_{24}O_8$: C, 54.2; H, 7.3. Found: C, 54.0; H, 7.1.

*Methyl 2,3,5,6-tetra-*O*-acetyl-α-*D*-mannofuranoside* (**4**). — A solution of methyl 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranoside (150 mg, 5.5 mmol) in aqueous acetic acid (10 ml, 70%) was heated at 90° for 30 min. Solvents were removed, and the residue was acetylated with acetic anhydride–pyridine, in the conventional manner, to give a mixture that was chromatographed [ethyl acetate–hexane (1 : 1)]. Methyl 5,6-di-*O*-acetyl-2,3-*O*-isopropylidene-α-D-mannofuranoside (58 mg, 34%) was eluted first, followed by **4** (70 mg, 36%) as an oil, $[\alpha]_D^{20}$ +105°; lit.[9] $[\alpha]_D^{20}$ +108°. N.m.r. data: τ 4.44 (dd, 1 H, $J_{3,4}$ 4, $J_{3,2}$ 5 Hz, H-3), 4.71 (o, 1 H, $J_{5,4}$ 9, $J_{5,6a}$ 6, $J_{5,6b}$ 2.5 Hz, H-5), 4.82 (dd, 1 H, $J_{2,1}$ 3, $J_{2,3}$ 5 Hz, H-2), 4.99 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.46 (dd, 1 H, $J_{6a,5}$ 2.5, $J_{6a,6b}$ 12 Hz, H-6a), 5.64 (dd, 1 H, $J_{4,3}$ 4, $J_{4,5}$ 9 Hz, H-4), 5.84 (dd, 1 H, $J_{6b,5}$ 6, $J_{6b,6a}$ 12 Hz, H-6b), 6.62 (s, 3 H, OMe), and 7.95, 7.96, and 8.0 (3 s, 12 H, 4 OAc).

*Ethyl 3-*O*-(2,3 : 5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**11**) *and 2-*O*-acetyl-3-*O*-(2,3 : 5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-glucofuranosyl m-chlorobenzoate* (**13**) *and its α-*D*-glucofuranosyl anomer* **14**. — The glycal **2** (340 mg, 0.8 mmol) was treated with *m*-chloroperbenzoic acid (140 mg, 0.8 mmol), as described for the preparation of **7** and **8**, and the product was chromatographed [ethyl acetate–hexane (3 : 2)] to give **2** (20 mg, 7%), and then a mixture of *m*-chlorobenzoates (15 mg, 3%) which was acetylated in the conventional manner with acetic anhydride–pyridine and chromatographed [p.l.c., ethyl acetate–hexane (1 : 1)] to give the faster-moving α-D anomer **14** as an oil (5 mg), $[\alpha]_D^{20}$ +94°, ν_{max} 1740 cm^{-1} (CO). Mass spectrum: *m/e* 629 and 627 (M^+ — Me). N.m.r. data: τ 1.94–2.7 (m, 4 H, aromatic H), 3.56 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.58 (dd, 1 H, $J_{2,1}$ 4.5, $J_{2,3}$ 3.5 Hz, H-2), 4.76 (s, 1 H, H-1′), 5.21 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3′), 5.36 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2′), 5.4–6.1 (m, 9 H, H-3,4,5,6a,6b,4′,5′,6′a,6′b), 8.01 (s, 3 H, OAc), and 8.55, 8.57, 8.64, 8.68, and 8.75 (5 s, 18 H, 6 Me).

Anal. Calc. for $C_{29}H_{36}ClO_{13}$ (M^+ — 15): 627.18. Found: 627.17.

The slower-moving β-D anomer **13** (8 mg) was an oil, $[\alpha]_D^{20}$ +20°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 629 and 627 (M^+ — Me). N.m.r. data: τ 2.01–2.7 (m, 4 H, aromatic H), 3.77 (s, 1 H, H-1), 4.23 (s, 1 H, H-2), 4.74 (s, 1 H, H-1′),

5.16 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3'), 5.33 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.5–6.1 (m, 9 H, H-3,4,5,6a,6b,4',5',6'a,6'b), 7.88 (s, 3 H, OAc), and 8.52, 8.56, 8.6, 8.62, and 8.74 (5 s, 18 H, 6 Me).

Anal. Calc. for $C_{29}H_{36}ClO_{13}$ (M^+ — 15): 627.18. Found: 627.17.

Further elution of the column gave an unidentified mixture (9 mg, 2%) followed by the main product **11** (239 mg, 62%) as an oil, $[\alpha]_D^{20}$ −8°, ν_{max} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 475 (M^+ — Me). N.m.r. data: τ 4.88 (s, 1 H, H-1'), 5.14 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.24 (dd, 1 H, $J_{3',2'}$ 5.5, $J_{3',4'}$ 4 Hz, H-3'), 5.42 (d, 1 H, $J_{2',3'}$ 5.5 Hz, H-2'), 5.6–6.1 (m, 12 H, H-2,3,4,5,6a,6b,4',5',6'a,6'b, CH_2Me), 6.9 (br s, 1 H, disappears on addition of D_2O, OH), 8.56, 8.57, 8.6, 8.63, 8.65, and 8.69 (6 s, 18 H, 6 Me), and 8.82 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal: Calc. for $C_{23}H_{38}O_{11}$: C, 56.3; H, 7.8. Found: C, 56.4; H, 7.8.

The acetate (**12**) of **11** was an oil, $[\alpha]_D^{19}$ −5°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 517 (M^+ — Me). N.m.r. data: τ 4.77 (s, 1 H, H-2), 4.87 (s, 1 H, H-1'), 5.10 (s, 1 H, H-1), 5.23 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3'), 5.41 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.5–6.1 (m, 9 H, H-3,4,5,6a,6b,4',5',6'a,6'b), ~6.4 (m, 2 H, CH_2Me), 7.95 (s, 3 H, OAc), 8.56, 8.58, 8.6, 8.64, 8.67, and 8.69 (6 s, 18 H, 6 Me), and 8.82 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{25}H_{40}O_{12}$: C, 56.4; H, 7.6. Found: C, 56.8; H, 7.7.

*1,2,3-Tri-*O*-acetyl-5,6-*O*-isopropylidene-β-*D*-glucofuranose* (**15**) *and its α anomer* **16**. — The glycal **1** (130 mg, 0.55 mmol) was treated with osmium tetraoxide (150 mg, 1 mmol) in dry pyridine (10 ml) for 10 min. Aqueous sodium metabisulphite (10 ml, 5%) was added and the solution was stirred for 30 min. Evaporation of solvents gave a product that was acetylated with acetic anhydride–pyridine, in the conventional manner, to give a mixture. Chromatography [ethyl acetate–hexane (1 : 1)] afforded the α-D-*gluco*-acetate **16** (34 mg, 17%) as an oil, $[\alpha]_D^{20}$ +53°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 331 (M^+ — Me). N.m.r. data: τ 3.63 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.42 (t, 1 H, $J_{3,4} = J_{3,2}$ 5 Hz, H-3), 4.79 (dd, 1 H, $J_{2,1}$ 4.5, $J_{2,3}$ 5 Hz, H-2), 5.6–6.2 (m, 4 H, H-4,5,6a,6b), 7.95 and 7.96 (2 s, 9 H, 3 OAc), and 8.63 and 8.7 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{15}H_{22}O_9$: C, 52.0; H, 6.4. Found: C, 52.0; H, 6.2.

Further elution gave **15** (59 mg, 30%) as an oil, $[\alpha]_D^{20}$ −5°, ν_{max} 1755 cm^{-1} (CO). Mass spectrum: *m/e* 331 (M^+ — Me). N.m.r. data: τ 3.91 (s, 1 H, H-1), 4.64 (br d, 1 H, $J_{3,4}$ 4, $J_{3,2}$ 1 Hz, H-3), 4.85 (br s, 1 H, $J_{2,3}$ 1 Hz, H-2), 5.6–6.1 (m, 4 H, H-4,5,6a,6b), 7.9 and 7.92 (2 s, 9 H, 3 OAc), and 8.63 and 8.69 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{15}H_{22}O_9$: C, 52.0; H, 6.4. Found: C, 52.2.; H, 6.5.

A solution of **15** (30 mg, 0.08 mmol) in aqueous acetic acid (10 ml, 70%) was heated at 60° for 10 min. The solvent was evaporated, and the residue was acetylated with acetic anhydride–pyridine, in the conventional manner, to give **5** (32 mg, 93%) as an oil that was identical (n.m.r. and i.r. spectra) with authentic 1,2,3,5,6-penta-*O*-acetyl-β-D-glucofuranose[8].

*1,2-Di-*O*-acetyl-3-*O*-(2,3 : 5,6-di-*O*-isopropylidene-α-D-mannofuranosyl)-5,6-*O*-isopropylidene-α-D-glucofuranose* (**17**), *-β-D-glucofuranose* (**18**), *and -α,β-D-manno-*

furanose (**19**). — Osmylation, hydrolyses, and acetylation of the glycal **2** (260 mg, 0.6 mmol), using the conditions described for glycal **1**, gave a product that was chromatographed [ethyl acetate–hexane (1 : 1)] to afford **17** (85 mg, 26%) as an oil, $[\alpha]_D^{20}$ +78°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 531 (M^+ — Me). N.m.r. data: τ 3.69 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.85 (s, 1 H, H-1'), 4.87 (t, 1 H, $J_{2,1} = J_{2,3}$ 5 Hz, H-2), 5.24 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3 Hz, H-3'), 5.41 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.48–6.2 (m, 9 H, H-3,4,5,6a,6b,4',5',6'a,6'b), 7.91 and 7.96 (2 s, 6 H, 2 OAc), and 8.56, 8.58, 8.6, 8.63, 8.64, and 8.67 (6 s, 18 H, 6 Me).

Anal. Calc. for $C_{25}H_{38}O_{11}$: C, 54.9; H, 7.0. Found: C, 54.6; H, 6.9.

Further elution gave **18** (45 mg, 14%) as an oil, $[\alpha]_D^{20}$ —6°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 531 (M^+ — Me). N.m.r. data: τ 3.95 (s, 1 H, H-1), 4.69 (s, 1 H, H-2), 4.81 (s, 1 H, H-1'), 5.21 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3 Hz, H-3'), 5.36 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.48–6.1 (m, 9 H, H-3,4,5,6a,6b,4',5',6'a,6'b), 7.92 (s, 6 H, 2 OAc), and 8.54, 8.57, 8.61, 8.63, and 8.66 (5 s, 18 H, 6 Me).

Anal. Calc. for $C_{25}H_{38}O_{11}$: C, 54.9; H, 7.0. Found: C, 54.6; H, 7.3.

Further elution gave an anomeric mixture of D-mannofuranoses **19** (20 mg, 6%) as an oil, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 531 (M^+ — Me).

Anal. Calc. for $C_{25}H_{38}O_{11}$: C, 54.9; H, 7.0. Found: C, 54.9; H, 7.0.

Deacetylation (MeOH–NaOMe) of **17**, **18**, and **19** (10 mg of each), followed by deacetylation (M H_2SO_4, 80°, 3 h), gave products that were shown by t.l.c. [2-propanol–ethyl acetate–toluene–water (50 : 25 : 12.5 : 10)] to contain, respectively, glucose and mannose, glucose and mannose, and mannose only.

*1,2,3,5,6-Penta-*O*-acetyl-α-*D*-glucofuranose* (**6**). — Deacetylation and acetylation of **16** (10 mg, 0.2 mmol), as described for **15**, gave the peracetate **6** (8 mg, 70%) as an oil, $[\alpha]_D^{20}$ +61°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 331 (M^+ — OAc). N.m.r. data: τ 3.55 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.45 (dd, 1 H, $J_{3,2}$ 3, $J_{3,4}$ 5 Hz, H-3), 4.77 (septet, 1 H, $J_{5,4}$ 8.5, $J_{5,6a}$ 3, $J_{5,6b}$ 6 Hz, H-5), 4.8 (dd, 1 H, $J_{2,3}$ 3, $J_{2,1}$ 4.5 Hz, H-2), 5.44 (dd, 1 H, $J_{6a,5}$ 3, $J_{6a,6b}$ 12 Hz, H-6a), 5.22 (dd, 1 H, $J_{4,3}$ 5, $J_{4,5}$ 8.5 Hz, H-4), 5.9 (dd, 1 H, $J_{6b,5}$ 6, $J_{6b,6a}$ 12 Hz, H-6b), and 7.89, 7.92, 7.94, and 7.98 (4 s, 15 H, 5 OAc).

Anal. Calc. for $C_{14}H_{19}O_9$ (M^+ — OAc): 331.103. Found: 331.106.

*Methyl 3-*O*-acetyl-2-deoxy-5,6-*O*-isopropylidene-β-*D*-*arabino*-hexofuranoside* (**20**) *and its* α-D *anomer* (**21**). — Mercuric acetate (190 mg, 0.6 mmol) was added to a solution of the glycal **1** (119 mg, 0.6 mmol) in methanol (10 ml), and the mixture was stirred at 25° for 10 min. An excess of sodium borohydride was added; after 5 min, the solution was filtered and the solvent was evaporated to leave an oil (45 mg, 30%), ν_{max}^{NaCl} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 203 (M^+ — Me). N.m.r. data: τ 4.83 and 4.96 (2 t, 2 H-1), 6.33 and 6.35 (2 s, 2 OMe, ratio ~3 : 1). The product was acetylated (pyridine–acetic anhydride) to give a mixture that was chromatographed [ethyl acetate–hexane (1 : 1)] to give **21** (11 mg, 7%) as an oil, $[\alpha]_D^{20}$ +37°, ν_{max}^{NaCl} 1745 cm^{-1} (CO). Mass spectrum: *m/e* 245 (M^+ — Me). N.m.r. data: τ 4.62 (m, 1 H, H-3), 4.92 (dd, 1 H, $J_{1,2a}$ 3, $J_{1,2b}$ 5 Hz, H-1), 5.7–6.18 (m, 4 H, H-4,5,6a,6b), 6.69 (s, 3 H,

OMe), ~7.8 (m, 2 H, H-2a,2b), 7.98 (s, 3 H, OAc), and 8.62 and 8.69 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{11}H_{17}O_6$ (M^+ — Me): 245.103. Found: 245.104.

Further elution gave **20** (30 mg, 20%) as an oil, $[\alpha]_D^{20}$ −72°, ν_{max} 1745 cm^{-1} (CO). Mass spectrum: *m/e* 245 (M^+ — Me). N.m.r. data: τ 4.62 (septet, 1 H, H-3), 5.0 (dd, 1 H, $J_{1,2a}$ 2, $J_{1,2b}$ 5 Hz, H-1), 5.6–6.08 (m, 4 H, H-4,5,6a,6b), 6.67 (s, 3 H, OMe), 7.66 (o, 1 H, $J_{2a,1}$ 2, $J_{2a,2b}$ 14, $J_{2a,3}$ 6 Hz, H-2a), 7.91 (sextet, 1 H, $J_{2b,1} = J_{2b,3} = 2$, $J_{2b,2a}$ 14 Hz, H-2b), 7.96 (s, 3 H, OAc), and 8.62 and 8.68 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{12}H_{20}O_6$: C, 55.4; H, 7.8. Found: C, 55.2; H, 7.6.

*Methyl 2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-*arabino*-hexofuranoside* (**22**). — A solution of the glycal **2** (520 mg, 1.2 mmol) in methanol (25 ml) was treated with mercuric acetate (385 mg, 1.2 mmol) and then reduced as described for the preparation of **20** and **21**, to give a mixture that was chromatographed [ethyl acetate–hexane (1:1)]. Starting material (22 mg, 4%) was first eluted, followed by **22** (190 mg, 33%) as a solid that crystallized from hexane; m.p. 97–99°, $[\alpha]_D^{20}$ −27°. Mass spectrum: *m/e* 445 (M^+ — Me). N.m.r. data: τ 4.91 (s, 1 H, H-1′), 5.04 (dd, 1 H, $J_{1,2a}$ 5.5, $J_{1,2b}$ 2 Hz, H-1), 5.24 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3 Hz, H-3′), 5.42 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2′), 5.5–6.1 (m, 9 H, H-3,4,5,6a,6b, 4′,5′,6′a,6′b), 6.69 (s, 3 H, OMe), ~7.8 (m, 2 H, H-2a,2b), and 8.57, 8.6, 8.63, 8.65, and 8.7 (5 s, 18 H, 6 Me).

Anal. Calc. for $C_{22}H_{36}O_{16}$: C, 57.4; H, 7.9. Found: C, 57.1; H, 7.8.

*(R)-1-(2-Furyl)-1,2-*O*-isopropylidene-ethane-1,2-diol, ethyl 2-bromo-3-*O*-(2-bromo-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranosyl)-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**37**), *ethyl 2-bromo-2-deoxy-5,6-*O*-isopropylidene-β-*D*-glucofuranoside* (**23**) *and its* α-*D* *anomer* (**24**). — *N*-Bromosuccinimide (675 mg, 3.8 mmol) and then ethanol (0.2 ml) were added to a solution of the glycal **1** (600 mg, 3.2 mmol) in dry acetonitrile (10 ml) at 0°. Evaporation of the solvent gave a residue that was chromatographed [ethyl acetate–hexane (1:3)] to give (*R*)-1-(2-furyl)-1,2-*O*-isopropylidene-ethane-1,2-diol (**38**; 30 mg, 6%), which was identical (i.r., n.m.r., and mass spectra) with an authentic sample[5].

Further elution gave the disaccharide **37** (32 mg, 3.5%) as an oil, $[\alpha]_D^{20}$ −37°, ν_{max} 3485 cm^{-1} (OH). Mass spectrum: *m/e* 563, 561, and 559 (M^+ — Me). N.m.r. data: τ 4.62 (s, 1 H, H-1 or H-1′), 4.85 (d, 1 H, *J* 1.5 Hz, H-1 or H-1′), 5.36–6.1 (m, 12 H, H-2,3,4,5,6a,6b,2′,3′,4′,5′,6′a,6′b), 6.24 (m, 2 H, CH_2Me), 8.56 and 8.64 (2 s, 12 H, 4 Me), and 8.83 (t, 3 H, *J* 6.5 Hz, $CH_2\mathit{Me}$).

Anal. Calc. for $C_{20}H_{32}Br_2O_9$: C, 41.7; H, 5.6; Br, 27.7. Found: C, 41.8; H, 5.7; Br, 27.3.

Further elution gave the β-*D*-glucoside **23** (280 mg, 28%) as an oil, $[\alpha]_D^{20}$ −36°, ν_{max} 3480 cm^{-1} (OH). Mass spectrum: *m/e* 297 and 295 (M^+ — Me). N.m.r. data: τ 4.79 (s, 1 H, H-1), 5.63 (m, 2 H, H-2,3), 5.72–6.1 (m, 4 H, H-4,5,6a,6b), 6.36 (m, 2 H, CH_2Me), 6.92 (br s, 1 H, disappears on addition of D_2O, OH), 8.56 and 8.62 (2 s, 6 H, 2 Me), and 8.8 (t, 3 H, *J* 6.5 Hz, $CH_2\mathit{Me}$).

Anal. Calc. for $C_{11}H_{19}BrO_5$: C, 42.5; H, 6.2; Br, 25.7. Found: C, 42.8; H, 6.3; Br 26.0.

The acetate **25** of **23** was an oil, $[\alpha]_D^{20}$ −21°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 339 and 337 (M^+ − Me). N.m.r. data: τ 4.63 (dd, 1 H, $J_{3,2}$ 2, $J_{3,4}$ 5 Hz, H-3), 4.78 (d, 1 H, $J_{1,2}$ 1 Hz, H-1), 5.46–6.0 (m, 5 H, H-2,4,5,6a,6b), 6.4 (m, 2 H, CH_2Me), 7.93 (s, 3 H, OAc), 8.61 and 8.68 (2 s, 6 H, 2 Me), and 8.81(t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{13}H_{21}BrO_6$: C, 44.2; H, 6.0; Br, 22.6. Found: C, 44.2; H, 6.1; Br, 22.8.

Further elution gave the α-D-glucoside **24** (32 mg, 3%) as an oil, $[\alpha]_D^{20}$ +69°, ν_{max} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 297 and 295 (M^+ − Me). N.m.r. data: τ 4.92 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.36 (t, 1 H, $J_{3,2} = J_{3,4}$ = 5 Hz, H-3), 5.6–6.6 (m, 7 H, H-2,4,5,6a,6b, CH_2Me), 7.08 (br s, 1 H, disappears on addition of D_2O, OH), 8.57 and 8.64 (2 s, 6 H, 2 Me), and 8.76 (t, 3 H, *J* 6.5 Hz, CH_2*Me*).

Anal. Calc. for $C_{11}H_{19}BrO_5$: C, 42.5; H, 6.2; Br, 25.7. Found: C, 42.8; H, 6.3; Br, 25.2.

The acetate **26** of **24** was an oil, $[\alpha]_D^{20}$ +66°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 339 and 337 (M^+ − Me). N.m.r. data: τ 4.34 (t, 1 H, $J_{3,2} = J_{3,4}$ 6 Hz, H-3), 4.97 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 5.6–6.1 (m, 5 H, H-2,4,5,6a,6b), 6.3 (m, 2 H, CH_2Me), 7.91 (s, 3 H, OAc), 8.63 and 8.74 (2 s, 6 H, 2 Me), and 8.75 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{12}H_{18}BrO_6$ (M^+ − Me): 337.029. Found: 337.030.

*Ethyl 2-bromo-2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-gluco- and -manno-furanoside* (**27**) *and 2-bromo-2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-α- and -β-*D*-glucofuranose* (**28**). — The glycal **2** (200 mg, 0.47 mmol) was treated with *N*-bromosuccinimide (180 mg, 1 mmol) in acetonitrile (10 ml), followed by the addition of ethanol (0.2 ml) at 0°, and the mixture was worked-up as described for the preparation of **23** and **24**, to give a residue that was chromatographed [ethyl acetate–hexane (1:1)] to give the mixture **27** (50 mg, 20%) as an oil. Mass spectrum: *m/e* 539 and 537 (M^+ − Me).

Further elution gave the anomeric mixture **28** (66 mg, 27%) as an oil, ν_{max} 3450 cm^{-1} (OH). Mass spectrum: *m/e* 511 and 509 (M^+ − Me).

Acetylation (pyridine–acetic anhydride) of **28** gave a mixture that was chromatographed [ethyl acetate–hexane (3:1)] to give the α-D isomer **30** (11 mg, 20%) as an oil, $[\alpha]_D^{20}$ +58°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 565 and 563 (M^+ − Me). N.m.r. data: τ 3.75 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.83 (s, 1 H, H-1'), 5.2 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3'), 5.4 (m, 2 H, H-2,2'), 5.54–6.2 (m, 9 H, H-3,4,5,6a,6b, 4',5',6'a,6'b), 7.88 (s, 3 H, OAc), and 8.54, 8.59, 8.61, 8.64, and 8.67 (5 s, 18 H, 6 Me).

Further elution gave the β-D isomer **29** (31 mg, 58%) as an oil, $[\alpha]_D^{20}$ +17°, ν_{max} 1755 cm^{-1} (CO). Mass spectrum: *m/e* 565 and 563 (M^+ − Me). N.m.r. data: τ 3.69 (s, 1 H, H-1), 4.85 (s, 1 H, H-1'), 5.24 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3'), 5.38 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.48–6.1 (m, 10 H, H-2,3,4,5,6a,6b,4',5',6'a,6'b), 7.95 (s, 3 H, OAc) and 8.55, 8.58, 8.61, 8.64, 8.67, and 8.68 (6 s, 18 H, 6 Me).

The high molecular weights of **28** and **29** gave rise to inaccurate mass determinations by m.s. Elemental analyses were also unsatisfactory.

*Ethyl 2-deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-*arabino*-hexofuranoside* (**33**). — A solution of **27** (25 mg, 0.04 mmol) in dry tetrahydrofuran (10 ml) was reduced with an excess of lithium aluminium hydride for 3 h at 25°. Work-up in the conventional manner, with chromatography [ethyl acetate–hexane (1 : 1)] of the residue, gave **33** (10 mg, 47%) as an oil, $[\alpha]_D^{20}$ −21°. Mass spectrum: *m/e* 459 (M^+ — Me). N.m.r. data: τ 4.89 (m, 2 H, H-1,1'), 5.22 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3'), 5.42 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2'), 5.56–6.1 (m, 9 H, H-3,4,5,6a,6b,4',5',6'a,6'b), ~6.3 (m, 2 H, CH_2Me), 7.8 (m, 2 H, H-2a,2b), 8.54, 8.56, 8.58, 8.62, and 8.74 (6 s, 18 H, 6 Me), and 8.74 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{22}H_{35}O_{10}$ (M^+ — Me): 459.223. Found: 459.220.

*Ethyl 2,3-anhydro-5,6-*O*-isopropylidene-β-*D*-mannofuranoside* (**39**) *and ethyl 2-deoxy-5,6-*O*-isopropylidene-β-*D*-*arabino*-hexofuranoside* (**31**). — A solution of the glycoside **23** (120 mg, 0.4 mmol) in tetrahydrofuran (5 ml) was reduced at 65° with an excess of lithium aluminium hydride. Work-up afforded an oil that was chromatographed [ethyl acetate–hexane (1 : 1)] to give starting material (25 mg, 21%), followed by **39** (50 mg, 56%) as an oil, $[\alpha]_D^{20}$ −54°. Mass spectrum: *m/e* 215 (M^+ — Me). N.m.r. data: τ 4.95 (s, 1 H, H-1), 5.6–6.4 (m, 8 H, H-2,3,4,5,6a,6b, CH_2Me), 8.58 and 8.65 (2 s, 6 H, 2 Me, and 8.77 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{10}H_{15}O_5$ (M^+ — Me): 215.092. Found: 215.092.

Further elution gave **31** (15 mg, 17%) as an oil, $[\alpha]_D^{20}$ −58°, ν_{max}^{NaCl} 3500 cm^{-1} (OH). Mass spectrum: *m/e* 217 (M^+ — Me). N.m.r. data: τ 4.87 (dd, 1 H, $J_{1,2a}$ 3, $J_{1,2b}$ 2 Hz, H-1), 5.3–6.7 (7 H, m, H-3,4,5,6a,6b, CH_2Me), 7.12 (br d, 1 H, disappears on addition of D_2O, OH), ~7.9 (m, 2 H, H-2a,2b), 8.57 and 8.63 (2 s, 6 H, 2 Me), and 8.82 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{10}H_{17}O_5$ (M^+ — Me): 217.108. Found: 217.108.

The acetate (**32**) of **31** was an oil, $[\alpha]_D^{20}$ −58°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 259 (M^+ — Me). N.m.r. data: τ 4.63 (septet, 1 H, H-3), 4.89 (dd, 1 H, $J_{1,2a}$ 2, $J_{1,2b}$ 6 Hz, H-1), 5.6–6.05 (m, 4 H, H-4,5,6a,6b), ~6.4 (m, 2 H, CH_2Me), 7.5–8.04 (m, 5 H, H-2a,2b and OAc), 8.61 and 8.67 (2 s, 6 H, 2 Me), and 8.81 (t, 3 H, *J* 7 Hz, CH_2*Me*).

Anal. Calc. for $C_{12}H_{19}O_6$ (M^+ — Me): 259.118. Found: 259.119.

The 2-deoxy derivative **32** was also prepared by reducing a solution of **25** (33 mg, 0.9 mmol) with an excess of tributylstannane in benzene (2 ml), containing α,α'-azobis(isobutyronitrile) (1 mg), at 60° for 1 h. The solvent was evaporated off, to leave a residue that was chromatographed [ethyl acetate–hexane (1 : 1)] to give **32** (23 mg, 88%).

*Ethyl 3-*O*-acetyl-2-deoxy-5,6-*O*-isopropylidene-α-*D*-arabino-hexofuranoside* (**34**). — Reduction of a solution of **26** (75 mg, 0.21 mmol) in benzene (2.5 ml) with an excess of tributylstannane in the presence of a trace of α,α'-azobis(isobutyronitrile), as described for the preparation of **32**, gave a residue that was chromatographed

[ethyl acetate–hexane (1:3)] to give **34** (40 mg, 70%) as an oil, $[\alpha]_D^{20}$ +34°, ν_{max} 1740 cm^{-1} (CO). Mass spectrum: *m/e* 259 (M^+ — Me). N.m.r. data (Varian EM-390 spectrometer, 90 MHz): τ 4.56 (m, 1 H, H-3), 4.77 (dd, 1 H, $J_{1,2a}$ 3, $J_{1,2b}$ 6 Hz, H-1), 5.6–6.05 (m, 4 H, H-4,5,6a,6b), ~6.4 (m, 2 H, CH_2Me), 7.75–7.9 (m, 2 H, H-2a,2b), 7.93 (s, 3 H, OAc), 8.59 and 8.68 (2 s, 6 H, 2 Me), and 8.8 (t, 3 H, *J* 7 Hz, CH_2Me).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.9; H, 8.1. Found: C, 56.7; H, 7.9.

*2-Deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-β-*D*-*arabino*-hexofuranosyl acetate* (**35**). — Debromination of **29** (31 mg, 0.05 mmol) with an excess of tributylstannane in benzene, as described for the preparation of **32**, gave a residue that was chromatographed [ethyl acetate–hexane (1:1)] to give **35** (26 mg, 98%) as a solid that crystallized from hexane; m.p. 112–113°, $[\alpha]_D^{20}$ −22°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 473 (M^+ — Me). N.m.r. data: τ 3.77 (dd, 1 H, $J_{1,2a}$ 1, $J_{1,2b}$ 6 Hz, H-1), 4.86 (s, 1 H, H-1′), 5.14 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 3.5 Hz, H-3′), 5.4 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2′), 5.5–6.2 (m, 9 H, H-3,4,5, 6a,6b,4′,5′,6′a,6′b), ~7.7 (m, 2 H, H-2a,2b), 7.97 (s, 3 H, OAc), and 8.56, 8.58, 8.63, 8.65, 8.67, and 8.68 (6 s, 18 H, 6 Me).

Anal. Calc. for $C_{23}H_{36}O_{11}$: C, 56.5; H, 7.4. Found: C, 56.3; H, 7.5.

*2-Deoxy-3-*O*-(2,3:5,6-di-*O*-isopropylidene-α-*D*-mannofuranosyl)-5,6-*O*-isopropylidene-α-*D*-*arabino*-hexofuranosyl acetate* (**36**). — Debromination of **30** (11 mg, 0.02 mmol) with an excess of tributylstannane in benzene, as described for the preparation of **32**, gave **36** (8 mg, 95%) as an oil, $[\alpha]_D^{20}$ +32°, ν_{max} 1750 cm^{-1} (CO). Mass spectrum: *m/e* 473. N.m.r. data: τ 3.65 (dd, 1 H, $J_{1,2a}$ 4.5, $J_{1,2b}$ 5 Hz, H-1), 4.81 (s, 1 H, H-1′), 5.22 (dd, 1 H, $J_{3',2'}$ 6, $J_{3',4'}$ 4 Hz, H-3), 5.42 (d, 1 H, $J_{2',3'}$ 6 Hz, H-2′), 5.48–6.18 (m, 9 H, H-3,4,5,6a,6b,4′,5′,6′a,6′b), ~7.7 (m, 2 H, H-2a,2b), 7.96 (s, 3 H, OAc), and 8.55, 8.59, 8.61, 8.65, 8.68, and 8.75 (6 s, 18 H, 6 Me).

Anal. Calc. for $C_{22}H_{33}O_{11}$ (M^+ — Me): 473.203. Found: 473.203.

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