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CARBON-13 AND PROTON NUCLEAR MAGNETIC RESONANCE STUDIES ON METHYL ALDOFURANOSIDES AND THEIR *O*-ALKYL DERIVATIVES*

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ABSTRACT

The effect of *O*-alkylation on the carbon-13 n m r. spectra of methyl pentofuranosides has been determined *O*-Alkylation of an OH group displaced the signal of the appended ^{13}C nucleus downfield, whereas the adjacent ^{13}C nuclei were, in most instances, shifted upfield to a smaller extent The effect of *O*-methylation was appreciably larger than *O*-isopropylation or *O*-glycosylation, but either *O*-methyl or *O*-isopropyl derivatives may be used as models for interpreting the spectra of furanoid oligo- and poly-saccharides, including the galactomannan of *Penicillium charlesii* The signal displacements are, to a large extent, comparable to those observed in the conformationally more stable mannopyranose series, so that they are insensitive to effects of steric distortion and population (or both) These effects occurred on 3-*O*-alkylation of methyl pentofuranosides, as appreciable changes in $J_{1,2}$ values in their p m r spectra were observed

DISCUSSION

Several recent studies have reported the shifts of carbon-13 nuclear magnetic resonance (^{13}C n m r) signals of sugars that occur on methylation of a single hydroxyl group[1–4]. The observed displacements can be of aid in interpreting ^{13}C n m r. spectra of oligosaccharides and polysaccharides, as shifts produced by *O*-glycosylation are apparently in the same direction and of a similar order of magnitude as those occurring on *O*-methylation[4–6] In the α- and β-D-mannopyranose series[4], *O*-methylation or *O*-glycosylation displaced, to an appreciable extent only the signals of ^{13}C nuclei positioned α and β relative to the substituent The shift values for methyl ethers were determined more readily than those of oligo- and poly-saccharides, and it was found that methylation of a hydroxyl group results in a downfield shift of 7–10 p p m of the signal of the substituted ^{13}C nucleus This was accompanied, in most instances, by upfield shifts of $\approx$1 p p m of the signals of the adjacent nuclei,

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when the hydroxyl group was equatorial. However, when the group was axial, the upfield shift was much greater, sometimes being as much as 4 p p m

In order to determine whether the signal displacements occur with the same regularity in furanosides (which can exist in numerous interconvertible conformational states[7]) and whether the interpretation of ^{13}C spectra of furanoid oligosaccharides and polysaccharides might be aided by the same approach, the ^{13}C n m r. spectra of a number of methyl pentofuranosides and their mono-*O*-methyl derivatives were compared.

TABLE I

ASSIGNMENT OF SIGNALS IN ^{13}C N M R SPECTRA OF METHYL PENTOFURANOSIDES IN D_2O (chemical shifts as δ_c compared with Me_4Si in p p m at 33°)[a]

Glycoside	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*OCH_3-1*
Methyl α-D-arabinofuranoside[8]	109 3	81 9	77 5	84 9	62 4	56 1
Methyl β-D-arabinofuranoside[8]	103 2	77 5	75 7	83 1	64 2	56 3
Methyl α-D-lyxofuranoside	109 1	77 0	72 0	81 3	61 2	56 9
Methyl β-D-lyxofuranoside	103.2	72 9	70 7	81 9	62 4	56 5
Methyl α-D-xylofuranoside	103 0	77 7	76 0	79 3	61 5	56 6
Methyl β-D-xylofuranoside	109 6	80 9	76 0	83 5	62 1	56 2
Methyl α-D-ribofuranoside[8]	104 2	72 1	70 8	85 5	62 6	56 5
Methyl β-D-ribofuranoside[8]	109 0	75 3	71 9	83 9	63 9	56 3

[a]Assignments and chemical shifts of these glycosides in water have been recently reported[28]

TABLE II

UPFIELD DISPLACEMENTS OF ^{13}C–C–^{2}H AND ^{13}C–^{2}H SIGNALS OF SUGARS[a] IN D_2O COMPARED WITH THOSE OF CORRESPONDING ^{13}C–C–^{1}H AND ^{13}C–^{1}H RESONANCES, RESPECTIVELY

Sugar	*Upfield displacement in p p m* [b]
Methyl α,β-D-lyxofuranoside-*3*-^{2}H	Not recorded
Methyl α,β-D-lyxofuranoside-*5*-$^{2}H_2$	C_α-4(0 10), C_β-4(0 12)
Methyl α,β-D-xylofuranoside-*3*-^{2}H	Not recorded
Methyl α,β-D-xylofuranoside-*5*-^{2}H	C_α-4(0 05), C_β-4(0 05), C_α-5, (0 50, *J* 22 Hz), C_β-5(0 47, *J* 20 Hz)
Methyl 3-*O*-isopropyl-α,β-D-xylofuranoside-*5*-^{2}H	C_α-4(0 09), C_β-4(0 08), C_α-5, (0 41, *J* 20 Hz), C_β-5(0 44, *J* 21 Hz)
Methyl 2-*O*-methyl-α,β-D-ribofuranoside-*2*-^{2}H	C_α-3(0 09), C_β-3(0 07)
Methyl 3-*O*-methyl-α,β D-ribofuranoside-*3*-^{2}H	C_α-2(0 07), C_β-2(0 09)
Methyl 3-*O*-methyl-α,β-D-ribofuranoside-*5*-^{2}H	C_α-4(0 03), C_β-4(0 03), C_β-5, (0 34; *J* 22 Hz), C_α-5 not recorded
Methyl 5-*O*-methyl-α,β-L-ribofuranoside-*2*-^{2}H	C_α-3(0 08), C_β-3(0 08)
Methyl 2-*O*-methyl-α,β-D-arabinofuranoside-*2*-^{2}H	C_α3(0 06), C_β3(0 05)
Methyl 2-*O*-methyl-α,β-D-arabinofuranoside-*5*-^{2}H	C_α4(0 05), C_β4(0 05)
Methyl 3-*O*-methyl-α,β-D-arabinofuranoside-*5*-^{2}H	C_α4(0 05), C_β4(0 05)
Methyl 5-*O*-methyl-α,β-D-arabinofuranoside-*5*-^{2}H	C_α-4(0 06), C_β-4(0 06)

[a]α and β subscripts refer to configuration at C-1 of the sugar [b]Unless otherwise stated, the signals of carbon atoms attached to deuterium disappeared.

TABLE III

DISPLACEMENTS OF ^{13}C SIGNALS IN METHYL *O*-ALKYL PENTOFURANOSIDES IN D_2O RELATIVE TO THOSE OF CORRESPONDING CARBON ATOMS IN THE PARENT METHYL PENTOFURANOSIDE

O-*Alkyl derivative of*	*Signal displacements in p p m* [a]				
	C-1	*C-2*	*C-3*	*C-4*	*C-5*
Methyl α-ribofuranoside					
2-*O*-methyl[b]	−1 1	+8 9	−1 4	+0 8	0
3-*O*-methyl[b]	−0 1	−0 3	+9 3	−1 9	+0 2
5-*O*-methyl[b]	−0 1	−0 2	0	−2 0	+10 6
2-*O*-isopropyl	−0 6	+5 0	−0 8	+0 7	+0 1
3-*O*-isopropyl	0	−0 7	+5 1	−1 5	−0 3
Methyl β-ribofuranoside					
2-*O*-methyl[b]	−2 4	+9 2	−0 8	+0 6	−0 3
3-*O*-methyl[b]	+0 2	−2 5	+9 4	−1 6	+0 1
5-*O*-methyl[b]	+0 1	−0 3	+0 3	−2 0	+11 0
2-*O*-isopropyl	−1 0	+5 4	−0 7	+0 7	−0 3
3-*O*-isopropyl	+0 1	−1 7	+5 1	−1 5	−0 4
Methyl α-arabinofuranoside					
2-*O*-methyl[b]	−2 0	+9 7	−2 0	−0 6	−0 4
3-*O*-methyl[b]	+0 3	−3 1	+10 3	−0 6	+0 3
5-*O*-methyl[b]	0	−0 2	+0 3	−1 8	+10 6
2-*O*-isopropyl	−1 1	+5 8	−1 2	−0 9	−0 3
Methyl β-arabinofuranoside					
2-*O*-methyl[b]	−1 5	+8 6	−1 1	+0 2	0
3-*O*-methyl[b]	+0 4	−0 4	+10 1	−0 6	+0 6
5-*O*-methyl[b]	+0 1	−0 3	+0.2	−2 1	+10 9
2-*O*-isopropyl	−0 9	+5 3 or +5 1	−0 9	−0 3 or −0 5	+0.2
Methyl α-lyxofuranoside					
2-*O*-methyl	−1 4	+9 6	−1 6	+0 5	0
2-*O*-isopropyl	−0 9	+5 6	−0 9	+0 5	0
Methyl β-lyxofuranoside					
2-*O*-methyl	−1 1	+8 7 or +9 4	−1 9	−0 4 or +0 3	−0 1
2-*O*-isopropyl	−0 4	+4 8	−0 9	+0 2	0
3-*O*-methyl	−0 1	+0 1	+7 9	−1 6	−0 3
Methyl α-xylofuranoside					
3-*O*-isopropyl[b]	−0 3	−1 2	+5 6	−0 7	+0 4
Methyl β-xylofuranoside					
3-*O*-isopropyl[b]	+0 1	−1 0	+6 1	−0 7	+0 3

[a] Minus is upfield, plus is downfield Assignments made by using deuterium isotope-effects [b] In these instances, the assignments were confirmed by using deuterated derivatives

In order to facilitate observation of such displacements, unambiguous assignments were made for the ^{13}C signals of the α- and β-anomers of methyl lyxofuranoside and methyl xylofuranoside by use of *C*-deuterated methyl pentofuranosides; the methyl ribofuranosides and methyl arabinofuranosides have been previously examined[8] Assignments were then based on the effect of the deuteron on the signal of the appended ^{13}C nucleus, which disappeared[9] or appeared as a triplet at higher field[10], and the effect on the signal(s) of the adjacent ^{13}C nucleus or nuclei, which were shifted upfield[4 8 11] by 0 03 to 0 12 p p m The complete interpretations of the spectra are presented in Table I and the values of the β-carbon shifts are summarized in Table II As may be seen from the present and previous data on methyl ribofuranosides and methyl arabinofuranosides[8], each sugar gives rise to a ^{13}C n m r spectrum displaying signals of C-1, C-4, C-2, C-3, C-5, and OCH_3-1, consecutively, proceeding from low to high field

The ^{13}C n m r spectra of some of the mono-*O*-methyl pentofuranosides were similarly interpreted by using deuterated analogues These analogues were the 2-, 3-, and 5-methyl ethers of methyl α,β-D-arabinofuranoside and the 2-, 3-, and 5-methyl ethers of methyl α,β-D-ribofuranoside The observed displacements of methoxyl signals (Table III) were found comparable to those of pyranosides, the main ones being of the *O*-methylated carbons atoms (+8 to +11 p p m)* and of the adjacent carbon atom(s) (mostly −1 to −3 p p m, some being as small as −0 3 p p m) These figures were sufficiently consistent that they could be used as a basis for interpreting the ^{13}C spectra of methyl 2-*O*-methyl-α,β-D-lyxofuranoside and methyl 3-*O*-methyl-α-D-lyxofuranoside

It is significant that no spectral changes occurred, even in such a "crowded" molecule as methyl 3-*O*-methyl-β-D-lyxofuranoside (four vicinal substituents above the ring), that would be attributable to distortions of a single conformer and/or variation of the percentages of populations of given conformers Accordingly, similar measurements were conducted with the conformationally larger *O*-isopropyl substituent, whose dimensions correspond more closely to those of a glycosyl group The 2- and 3-isopropyl ethers of methyl α,β-D-ribofuranoside, and also methyl 2-*O*-isopropyl-α,β-D-lyxofuranoside, were prepared The displacements of their ^{13}C signals relative to the parent methyl pentofuranoside could be readily measured without use of deuterated derivatives, as the signals are comparatively well separated The observed values are from +4 8 p p m to +5 8 p p m for the signal of the *O*-alkylated ^{13}C nucleus and −0 4 to −1 5 p p m for those of the adjacent nuclei, no other marked displacements being observed On proceeding from the *O*-methyl to the *O*-isopropyl derivative of a given methyl glycoside, it may be seen from Table III that the α and β ^{13}C signal-displacements are both smaller in magnitude If this consistency were also true for *O*-glycosylation, it might be used for interpreting the ^{13}C n m r spectra of oligo- and poly-saccharides, as the β-displacement could be estimated once the α-displacement is known

*A positive value denotes a downfield shift and a negative value an upfield one

An investigation of the ^{13}C signal-displacements occurring on *O*-glycosylation of furanosides was somewhat curtailed because reference compounds are not readily available The study was limited to 6-*O*-α- and β-L-arabinofuranosyl-D-glucose[12], "galactocarolose" (an extracellular polysaccharide from *Penicillium charlesii* containing 5-*O*-substituted β-D-galactofuranosyl and mannopyranosyl residues), and two derived oligosaccharides obtained by partial acid hydrolysis[13] Four galactose-containing oligosaccharides were formed, originally designated di-, tri-, tetra-, and pentasaccharide[13] The di- and tetra-saccharide have furanosyl non-reducing end-groups as their ^{13}C spectra showed C-1 signals at δ_c 101 9 and 96 0, corresponding to those of β- and α-D-galactofuranose (δ_c 102 0 and 96 0, respectively) The spectra also showed a C-1 signal at δ_c 108 0, arising from the other β-furanosyl C-1 atoms As may be seen from Fig 1, the ^{13}C n m r spectrum of the galactotetraose lends itself readily to interpretation in terms of signal displacements occurring on *O*-galactosylation of a β-D-galactofuranose moiety These results, and others obtained from the arabinofuranosyl disaccharides, are compiled in Table IV

The presence of two, low-field C-1 signals in the ^{13}C n m r spectrum of the galactomannan from *P charlesii* is unexpected The main one (at δ_c 108 0) evidently arises from non-reducing β-D-galactofuranosyl end-groups and 5-*O*-substituted β D-galactofuranosyl residues, by analogy with the spectrum of the galactotetraose However, a minor signal, 0 9 p p m to lower field, indicates the presence of another type of β-D-galactofuranosyl group, possibly the one attached to the mannan portion of the molecule Further evidence for this possibility was obtained from the ^{13}C spectrum of the "pentasaccharide" The C-1 region showed, in addition to the signal at δ_c 108 0, two signals at δ_c 97 5 and 93 4, corresponding in their chemical shifts to those of α- and β-D-galactose, respectively Thus the reducing end has a pyranose and not the expected furanose structure The exact structure of the "pentasaccharide", and the question of whether its reducing end-group arises from a galactofuranose structure, will receive further attention

From the foregoing data, it appears that the chemical shifts of the ^{13}C signals are insensitive to any conformational or population effects that might occur on *O*-alkylation of pentofuranosides, molecules that are relatively "crowded" compared with pyranosides Such effects could be extremely complex, it has been pointed out by Durette and Horton[7] that the pentofuranosides may readily exist in two or more conformers as the energy barriers between them are small (3–4 kcal mol^{-1}) *O*-Alkylation could either alter the percentages of each conformer, or steric compression might cause distortion of the ring of one or more conformers However, either of these effects could affect the value of the spin–spin coupling between H-1 and H-2 that is observed in the time-averaged proton spectra As may be seen later, and in Table V, the spin–spin coupling value may be modified on *O*-alkylation

As would be implied by the work of Karplus, especially in the paper where his generalized equation was formulated[14], 2-*O*-alkylation of methyl pentofuranosides could well affect the vicinal coupling-constant of H-1, even without conformational modification However, differences in the electronegativity of the substituent should

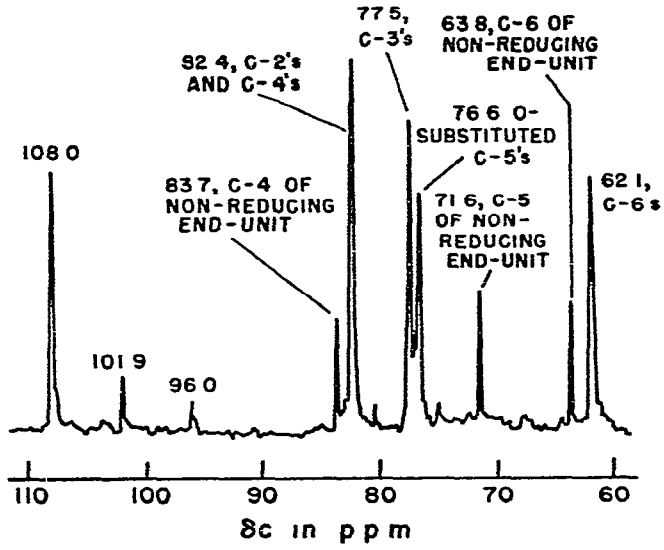

Fig 1. ^{13}C n m.r. spectrum of the (1→5) linked β-D-galactofuranose tetrasaccharide from *Penicillium charlesii* galactomannan[29] in D_2O

TABLE IV

CHEMICAL SHIFTS OF ^{13}C SIGNALS IN VARIOUS GLYCOFURANOSE DERIVATIVES IN D_2O, AND DISPLACEMENTS (IN PARENTHESES) ON *O*-ALKYLATION, IN P P M

Chemical shifts (displacements), p p m						*Chemical shifts (displacements), p p m*					
C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
Methyl β-D-galactofuranoside						*Galactotetraose, non-reducing end-group*					
109 2	81 9	77 8	84 0	72 0	63 9	108 0	82 4	77 5	83 7	71 6	63 8
Methyl 5-O-methyl-β-D-galactofuranoside						*Middle residues of galactotetraose*					
109 0	81 8	77 8	83 4	81 8	60 9	108 0	82 4	77 5	82 4	76 6	62 1
(−0.2)	(−0 1)	(0)	(−0 6)	(+9 8)	(−3 0)	(0)	(0)	(0)	(−1 3)	(+5 0)	(−1 7)
β-D-Arabinofuranose						*α-D-Arabinofuranose*					
96 2						102 1					
6-O-β-L-Arabinofuranosyl-α,β-D-glucose						*6-O-α-L-Arabinofuranosyl-α,β-D-glucose*					
101 9						108 9					
(+5 7)						(+6 8)					
β-D-Galactofurarose											
102 0											
Galactotetraose, non-reducing end-groups and middle residues											
108 0											
(+6 0)											

TABLE V

VICINAL SPIN–SPIN COUPLING VALUES OF H-1 SIGNALS OF METHYL PENTOFURANOSIDES AND THEIR 3-*O*-ALKYL DERIVATIVES IN D_2O

Glycoside	*Coupling value, Hz*
Methyl α-D-ribofuranoside	3 8
Methyl 3-*O*-methyl-α-D-ribofuranoside	4 5
Methyl 3-*O*-isopropyl-α-D-ribofuranoside	4 4
Methyl β-D-ribofuranoside	1 3
Methyl 3-*O*-methyl-β-D-ribofuranoside	1 2
Methyl 3-*O*-isopropyl-β-D-ribofuranoside	0 6
Methyl β-D-lyxofuranoside	4 1
Methyl 3-*O*-methyl-β-D-lyxofuranoside	4 7
Methyl α-D-xylofuranoside	3 4
Methyl 3-*O*-methyl-α-D-xylofuranoside	4 6
Methyl 3-*O*-isopropyl-α-D-xylofuranoside	4 3
Methyl β-D-xylofuranoside	1.1
Methyl 3-*O*-methyl-β-D-xylofuranoside	1 2
Methyl 3-*O*-isopropyl-β-D-xylofuranoside	1 8

not affect the coupling of H-1 to H-2 in the methyl 3-*O*-alkylpentofuranosides (Table V) The observed changes in spin–spin coupling (obtained at 70° to afford better resolution) in each series are equivalent to about 5–7° in terms of the time-averaged dihedral angle between H-1 and H-2, but whether this is caused by population effects, distortion of the ring, or both, is not yet clear

EXPERIMENTAL

Carbon-13 magnetic resonance spectroscopy — The ^{13}C n m r spectra were obtained by procedures identical to those described previously[4], except that a 16 K (instead of an 8 K) memory was used in the Fourier-transform experiments, and the operating temperature was 33° The chemical shifts are expressed as δ_c, compared with the shift of external tetramethylsilane, determined by measurement in a capillary in a tube containing D_2O, which served as a ^2H lock The offset, thus determined, was 32374 Hz, and this value was used in spectral measurements of sugars in D_2O.

Preparation of reference compounds

The ^{13}C n m r spectra of methyl glycosides and their derivatives were frequently obtained from anomeric mixtures In most instances, little difficulty was experienced in differentiating the signals of each anomer, as the minor component existed in small proportion and the configuration of the major one could be assigned from the specific rotation of the mixture In two examples, however, methyl 2-*O*-isopropyl-α,β-D-xylofuranoside and methyl 2-*O*-methyl-α,β-D-arabinofuranoside, the proportions were approximately equimolar when methanolic hydrogen chloride was used as reagent, and the components were resolved by column chromatography and their configurations determined from the relative specific rotations

The methyl 2-*O*-alkyl-α,β-arabinofuranosides or -lyxofuranosides, obtained by using cold methanolic hydrogen chloride, were treated successively with sodium metaperiodate and barium hydroxide to remove pyranosides The methyl 3-*O*-alkyl-α,β-pentofuranosides did not contain any pyranosides, as shown by refluxing in methanolic hydrogen chloride In each instance the product gave rise to new ^{13}C signals, which were those of pyranosides

The reference compounds were prepared by conventional routes, as described in the following experimental details Chromatographic solvents are v/v

Methyl 2-O-methyl-α,β-D-arabinofuranoside and their 2-^2H derivatives — 3-*O*-Methyl-D-glucose (1 0 g) was dissolved in water (2 ml), acetic acid (50 ml) was added, and lead tetraacetate (1 2 molar equivalents) introduced with stirring After 15 min, an excess of water was added The solution was then deionized and evaporated to a syrup that was dissolved in water (50 ml) The solution was maintained overnight at 100° to hydrolyze formic esters and the resulting 2-*O*-methyl-D-arabinose was converted directly into a mixture of methyl glycosides by action of cold, 0 5% hydrogen chloride in methanol (35 ml) After 18 h the solution was neutralized (silver carbonate) and evaporated, and the methyl pyranoside components were decomposed by addition of sodium metaperiodate (1 4 g) in water (50 ml) The solution was deionized, barium hydroxide (1 g) was added, and the mixture was maintained for 1 h at 100° Deionization, followed by evaporation gave methyl 2-*O*-methyl-α,β-D-arabinofuranoside (0 45 g)

Fractionation on a column of silicic acid (eluant 50.1, chloroform–methanol) gave the α anomer (149 mg), $[\alpha]_D^{25}$ +110° (*c* 1 0, water), p m r data (D_2O, 70°): δ 5 57, *J* 1 8 Hz (H-1)

Anal Calc for $C_7H_{14}O_5$. C, 47.18, H, 7 92 Found C, 47 07, H, 7 76

The bis(*p*-nitrobenzoate), after two recrystallizations from ethanol–hexane, had m p 113–114°, $[\alpha]_D^{25}$ +90° (*c* 0 7, chloroform)

Anal Calc for $C_{21}H_{20}N_2O_{11}$ C, 52 94, H, 4 23, N, 5 88 Found C, 52 98, H, 4 58, N, 5 80

The second fraction consisted of the β anomer (153 mg) which, from ethanol–hexane, had m p 49–50°, $[\alpha]_D^{25}$ −132° (*c* 0 8, water), p m r data (D_2O 70°). δ 5 64 *J* 4 4 Hz (H-1)

Anal Calc for $C_7H_{14}O_5$ C, 47 18, H, 7 92 Found. C, 46 94, H, 7 81

Methyl 2-*O*-methyl-α,β-D-arabinofuranoside-*2-^2H* was similarly prepared from *3-O*-methyl-D-glucose-*3-^2H*, which had been obtained in turn from 1,2·5,6-di-*O*-isopropylidene-α-D-glucofuranose-*3-^2H*[15]

Methyl 2-O-isopropyl-α,β-D-arabinofuranoside. — 2-*O*-Isopropyl-β-D-arabinose was prepared from 3-*O*-isopropyl-D-glucose[16] by the procedure outlined for the preparation of 2-*O*-methyl-D-arabinose from 3-*O*-methyl-D-glucose, yield 75% It had m p 109° (from ethyl acetate–hexane), $[\alpha]_D^{25}$ −94° → −83° (constant value, *c* 0.6, water)

Anal Calc for $C_8H_{16}O_5$. C, 49 99, H, 8 39 Found, C, 49 74, H, 8 09

The methyl glycosides were obtained as outlined for the 2-*O*-methyl derivatives

and the $[\alpha]_D^{25}$ +50° (*c* 0 3, water), indicated that it consisted mainly of the α anomer P m r data (D_2O, 70°) δ 5 44, *J* 1 2 Hz (H-1)

Anal Calc. for $C_9H_{18}O_5$ C, 52 41; H, 8.80 Found: C, 51 95; H, 8 58

Methyl 5-O-methyl-α,β-D-arabinofuranoside and the 5-²H derivative of its L-enantiomer. — Methyl 2,3-di-*O*-benzyl-α-D-arabinofuranoside was prepared by the method of Glaudemans and Fletcher[17] A portion (1 g) was methylated by Purdie's method and the product debenzylated hydrogenolytically with 5% palladium on charcoal in acetic acid to give methyl 5-*O*-methyl-α-D-arabinofuranoside, $[\alpha]_D^{25}$ +92° (*c* 0 3, water)

Anal. Calc for $C_7H_{14}O_5$· C, 47 18, H, 7 92 Found. C, 46 81, H, 7 77

It was converted into an α,β-anomeric mixture by refluxing in 0 5% methanolic hydrogen chloride for 30 min

Methyl 5-*O*-methyl-α,β-L-arabinofuranoside-*5-²H* was prepared similarly, starting from L-arabinose-*5-²H* This was prepared from a syrup (1 0 g) containing mainly methyl β-D-galactofuranoside, prepared from D-galactose by the action of cold 0 5% hydrogen chloride in methanol The glycoside was treated with 1 1 molar equivalents of sodium metaperiodate and, after 3 h, the solution was deionized Sodium borodeuteride (2 0 g) was then added and after 1 h the mixture was processed as before The product was hydrolyzed with 0 15M sulfuric acid for 2 h at 100°, providing L-arabinose-*5-²H* (0 27 g, from ethanol); m p 156–159°

Methyl 3-O-methyl-α,β-D-arabinofuranoside and the 5-²H derivative of its L-enantiomer — Methyl 5-*O*-trityl-α-D-arabinofuranoside[17] (1 0 g) was shaken with silver oxide (3 g) in methyl iodide (9 ml) for 6 h T l c on silica gel (50.1 chloroform–ethanol) showed that mono-*O*-methylation had taken place The mixture was diluted with dichloromethane, filtered, and the filtrate evaporated The trityl group was removed by heating in 80% aqueous acetic acid (25 ml) for 15 min at 100° and the solution was evaporated. The residue was chromatographed on a column of silicic acid (50·1 chloroform–methanol) and the fraction corresponding to methyl *O*-methyl-arabinofuranosides (0 50 g) isolated ^{13}C N m r spectroscopy showed that the product was mainly the 2-*O*-methyl derivative, but other signals (3-*O*-methyl derivative) were also detected

A mixture containing methyl 3-*O*-methyl-β-D-arabinofuranoside was obtained by hydrolysis of the glycoside, followed by treatment for 18 h with cold 0 5% hydrogen chloride in methanol (18 h)

The experiments were repeated with methyl 5-*O*-trityl-α-L-arabinofuranoside-*5-²H* (from methyl β-D-galactofuranoside) as starting material

Methyl 5-O-methyl-α,β-D-ribofuranoside-2-²H — Mixed methyl 2,3-*O*-benzylidene-β-L-arabinopyranosides[18] (1 20 g) were oxidized in dimethyl sulfoxide (10 ml) containing phosphorus pentaoxide (0 5 g) After 2 days, chloroform (250 ml) was added, and the solution was washed 3 times with equal volumes of ice–water The product (0 91 g) obtained on evaporation gave on t l c (50 1 chloroform–ethanol, 50% sulfuric acid as spray) a dark-brown spot moving faster than the starting material The presumed ketone was reduced with sodium borodeuteride (0 3 g) in

methanol (10 ml) maintained at −20° After 1 h, the solution was evaporated and dispersed between chloroform and water. The chloroform layer was evaporated to a syrup that was partially hydrolyzed in 80% aqueous acetic acid (20 ml) for 1 h at 100°. Evaporation gave a syrup that crystallized, and recrystallization from ethanol gave methyl β-L-ribopyranoside-2-^2H (0 27 g), m p. 81–84°, $[\alpha]_D^{25}$ +113° (*c* 0.4, water).

Anal Calc for $C_6DH_{11}O_5$. C, 43 63; H+D, 7 93. Found: C, 43.71; H+D, 7.74.

The glycoside (0 15 g) was hydrolyzed in 0 15M sulfuric acid for 3 h at 100° and following neutralization (barium carbonate) the resulting L-ribose-2-^2H was converted into methyl 5-*O*-methyl-α,β-L-ribofuranoside by the method of Woods *et al* [19]

Methyl 2-O-methyl-α,β-D-ribofuranoside-2-^{2}H and the 3-^{2}H and 5-^{2}H derivatives of methyl 3-O-methyl-α,β-D-ribofuranoside — 2-*O*-Methyl-D-ribose and 3-*O*-methyl-D-ribose were prepared according to the methods of Haga *et al* [20] and converted into their methyl α,β-furanosides by the action of cold, 0 5% hydrogen chloride in methanol for 1 h P m r data (D_2O, 70°) for the 3-*O*-methyl derivatives: δ_α 5 56 *J* 4 5 Hz; δ_β 5 50 *J* 1 2 Hz (H-1)· for the 2 *O*-methyl derivatives δ_α 5 68, *J* 4 3 Hz, δ_β 5 68, *J* 1 8 Hz (H-1) Methyl 2-*O*-methyl-α,β-D-ribofuranoside-2-^2H and methyl 3-*O*-methyl-α,β-D-ribofuranoside-3-^2H were obtained by using 1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose-3-^2H (ref 15) as starting material instead of its non-deuterated counterpart The crystalline bis(*p*-nitrobenzoate) of methyl 3-*O*-methyl-β-D-ribofuranoside-3-^2H (from ethyl acetate–hexane) had m p. 141–142°, $[\alpha]_D^{25}$ +14° (*c* 0 7, chloroform)

Anal Calc for $C_{21}DH_{19}N_2O_{11}$: N, 5.87 Found. N, 5.71.

Methyl 3-*O*-methyl-α,β-D-ribofuranoside-5-^2H was prepared by the method of Haga *et al* [20] except that, following periodate oxidation of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-allofuranose, the product was reduced with sodium borodeuteride instead of with sodium borohydride.

Methyl 2-O-isopropyl-α,β-D-ribofuranoside — 1,2·5,6-Di-*O*-isopropylidene-α-D-allofuranose[15] (0 45 g) was shaken for 6 days in 2-iodopropane (4 ml) and *N*,*N*-dimethylformamide (4 ml) containing silver oxide (4 g) The product obtained by filtration and evaporation was fractioned on a column of silicic acid (1 1 chloroform–hexane) to give syrupy 3-*O*-isopropyl-1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (0 38 g); $[\alpha]_D^{25}$ +84° (*c* 1 2, chloroform).

Anal Calc for $C_{15}H_{26}O_6$. C, 59 58, H, 8 67 Found· C, 59 13; H, 8 43

3-*O*-Isopropyl-1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (0 15 g) was heated in 0 1M sulfuric acid (5 ml) containing methanol (2 ml) on a steam bath until all of the methanol had evaporated and then for 1 h thereafter The solution was neutralized (barium carbonate), and evaporated to give syrupy 3-*O*-isopropyl-α,β-D-allose (0 12 g), $[\alpha]_D^{25}$ +14° (*c* 0 4, water)

Anal Calc for $C_9H_{18}O_6$. C, 48 64, H, 8 16 Found. C, 48.15, H, 8 02

The phenylosazone of 3-*O*-isopropyl-D-allose had m p 173–177°.

Anal. Calc for $C_{21}H_{28}N_4O_4$· N, 13 99. Found· N, 13 72

3-*O*-Isopropyl-D-allose (0.10 g) was converted quantitatively into 2-*O*-iso-

propyl-D-ribose $[\alpha]_D^{25}$ −25° (*c* 0 3, methanol) by oxidation with lead tetraacetate by the method already described

Anal. Calc for $C_8H_{16}O_5$: C, 49 99, H, 8 39. Found: C, 47 45, H, 7.83.

The derived *p*-tolylsulfonhydrazone had m p 146–147° (from methanol)

Anal Calc for $C_{15}H_{23}N_2O_6S$ N, 7 80 Found N, 7 64

The methyl furanosides, $[\alpha]_D^{25}$ 0° (*c* 0 4, water), were prepared by the action of cold 0 5% methanolic hydrogen chloride for 2 h, p m r data (D_2O, 70°) δ_α 5 29, *J* 4.1 Hz, δ_β 5 19, *J* 2 0 Hz (H-1)

Methyl 3-O-isopropyl-α,β-D-ribofuranoside. — 3-*O*-Isopropyl-1,2·5,6-di-*O*-isopropylidene-α-D-allofuranose (0 15 g) was shaken for 1 h in water–methanol (10 ml 3 ml) containing Amberlite IR-120 (H^+ form) Filtration and evaporation of the filtrate gave 3-*O*-isopropyl-1,2-*O*-isopropylidene-α-D-allofuranose (0 10 g, from ether–hexane); m p 98–99°, $[\alpha]_D^{25}$ +96° (*c* 0 3, chloroform)

Anal Calc for $C_{12}H_{22}O_6$: C, 54 94, H, 8 46 Found C, 54 92, H, 8 27

3-*O*-Isopropyl-1,2-*O*-isopropylidene-α-D-allofuranose (80 mg) was oxidized with sodium metaperiodate (150 g) in water (20 ml) for 3 h The solution was deionized, sodium borohydride (30 g) was added to the filtrate, and removal of the reagent in the conventional way provided 3-*O*-isopropyl-1,2-*O*-isopropylidene--α-D-ribo-furanose (55 mg), $[\alpha]_D^{25}$ +75° (*c* 0 4, chloroform)

Anal Calc for $C_{11}H_{20}O_5$· C, 56 88, H, 8 68 Found C, 57 21, H, 8 32

Hydrolysis under the conditions already described gave 3-*O*-isopropyl-D-ribose (43 mg), $[\alpha]_D^{25}$ 0° (*c* 0 4, water)

Anal Calc for $C_8H_{16}O_5$. C, 49 99, H, 8 39 Found. C, 49 44, H, 8 22

The methyl furanosidic mixture, $[\alpha]_D^{25}$ +20° (*c* 0 2, water), was obtained by using 0 5% methanolic hydrogen chloride for 2 h at room temperature, p m r data (D_2O, 70°)· δ_α 5 57, *J* 4 4 Hz, δ_β 5 50, *J* 0 6 Hz (H-1)

Methyl α,β-D-lyxofuranoside-3-^{2}H — 1,2.5,6-Di-*O*-Isopropylidene-α-D-galactofuranose-*4*-^2H (1 0 g) was obtained by the method of Paulsen and Behre[21], except that sodium borodeuteride was used as a reagent in place of sodium borohydride. It was benzylated by shaking it overnight in α-bromotoluene (4 0 liters) and *N,N*-dimethylformamide (4 0 ml) containing silver oxide (4 g) The product obtained following dilution with dichloromethane, filtration, and evaporation of the filtrate was hydrolyzed in 1,4-dioxane (2 ml) containing 0 5M sulfuric acid (2 ml) for 1 h at 100° The hydrolyzate was neutralized (barium carbonate), evaporated, and the residue partitioned between water and benzene Deionization of the aqueous layer followed by evaporation provided syrupy 3-*O*-benzyl-D-galactose-*4*-^2H (0 47 g), $[\alpha]_D^{25}$ +72° (*c* 0 5, water)

Anal Calc for $C_{13}DH_{17}O_6$· C, 57 55; H+D 7 06 Found C, 57 72, H+D, 6 78

The phenylosazone (from benzene) had m p. 159–160°.

Anal Calc for $C_{25}DH_{27}N_4O_4$ N, 12 21. Found N, 11 89.

Oxidation of 3-*O*-benzyl-D-galactose-*4*-^2H with lead tetraacetate, by the method already described, gave 2-*O*-benzyl-D-lyxose-*3*-^2H in quantitative yield. Crystallization

from ethyl acetate gave the α anomer, m p 78–80°, $[\alpha]_D^{25}$ 0° → −4° (*c* 0 3, water; constant value)

Anal. Calc for $C_{12}DH_{15}O_5$. C, 59 74, H+D, 7 10 Found C, 59 57, H+D, 6 89

Debenzylation with 5% palladium on charcoal in acetic acid provided D-lyxose-*3-*^2H (from ethanol), m p 110–114°

Anal Calc for $C_5DH_9O_5$ C, 39 73, H+D, 7 33 Found C, 39 56, H+D, 7 01

A mixture of the four possible methyl glycosides was obtained by the action of 0 5% methanolic hydrogen chloride for 5 h

*Methyl α,β-*D-*lyxofuranoside-*5-$^2H_2$ — Methyl α,β-D-lyxofuranoside (1 g), obtained via its 5-*O*-trityl derivative (see later), was dissolved in water (1 ml) containing a suspension of activated platinum (0 5 g) The temperature was maintained at 60°, air was bubbled through, and sodium hydrogencarbonate (0 51 g) was added gradually during 3 h After 18 h, Amberlite IR-120 (H^+) was added, the mixture was filtered, and Dowex 1-X8 (hydrogencarbonate) was added to the filtrate to absorb acidic material The acids were regenerated from the filtered resin by shaking in dilute formic acid The regenerated syrup was dissolved in 0 5% methanolic hydrogen chloride (10 ml), and the solution refluxed for 10 min, neutralized (silver carbonate), and evaporated The resulting methyl ester (0 27 g), was reduced in methanol (5 ml) containing sodium borodeuteride (0 10 g) and 0 1M sodium methoxide n methanol (1 ml) After 18 h, the solution was processed as before and the product fractionated on a cellulose column (7 2 benzene–ethanol) The resulting methyl α,β-D-lyxofuranoside-*5-*$^2H_2$ (0 13 g) had $[\alpha]_D^{25}$ +108° (*c* 0 5, water)

Anal Calc for $C_6D_2H_{16}O_5$ C, 43 37, H+D, 8 49 Found C, 42 90, H+D, 8 34

*The α and β anomers of methyl 5-*O*-trityl-*D*-lyxofuranoside* — D-Lyxose (5 g) was shaken in 0 5% methanolic hydrogen chloride (100 ml) for 3 h The solution was neutralized (silver carbonate) and the filtrate evaporated to a syrup Examination by ^{13}C n m r spectroscopy showed that it consisted mainly of methyl α-D-lyxofuranoside, with smaller proportions of the other three methyl lyxosides

A portion of the glycosidic mixture (1 0 g) was dissolved in pyridine (20 ml) containing chlorotriphenylmethane (1.3 molar equivalents) and the mixture was maintained for 18 h at 80° It was then added to aqueous sodium hydrogencarbonate, and the mixture extracted with chloroform The extract was evaporated to a syrup and chromatography on a column of silicic acid (3 2 chloroform–hexane) provided methyl 5-*O*-trityl-α-D-lyxofuranoside (0 95 g), $[\alpha]_D^{25}$ +51° (*c* 1 3, chloroform)

Anal Calc for $C_{45}H_{26}O_5$ C, 73 87, H, 6 45 Found C, 73 39, H, 6 22

Methyl 5-*O*-trityl-β-D-lyxofuranoside, $[\alpha]_D^{25}$ −18° (*c* 4 0, chloroform), was prepared in 63% yield from methyl β-D-lyxofuranoside[22], by the method already outlined for the α anomer

Anal Calc for $C_{25}H_{26}O_5$. C, 73 87, H, 6 45. Found. C, 73 61, H, 6 35

*Methyl 2-*O*-methyl-α-*D*-lyxofuranoside* — Methyl 5-*O*-trityl-α-D-lyxofuranoside (0 50 g) was partially methylated by shaking for 12 h in iodomethane (5 ml) con-

taining silver oxide (0 5 g) Filtration followed by evaporation of the filtrate provided the 2-*O*-methyl derivative (0 15 g) having $[\alpha]_D^{25}$ +29° (*c* 1 6, chloroform)

Anal. Calc for $C_{26}H_{28}O_5$ C, 74 26, H, 6 71 Found: C, 73 81, H, 6 82

Methyl 2-*O*-methyl-5-*O*-trityl-α-D-lyxofuranoside (0 4 g) was partially hydrolyzed for 20 min in 80% aqueous acetic acid (5 ml) at 100°. The residue obtained on evaporation was partly dissolved in water, which was extracted 4 times with chloroform Evaporation of the extract provided methyl 2-*O*-methyl-α-D-lyxofuranoside (0 18 g), $[\alpha]_D^{25}$ +122° (*c* 0 2, water), which was shown to be free of the 3-methyl ether by ^{13}C n m r spectroscopy

Anal Calc for $C_7H_{14}O_5$. C, 47.18, H, 7 92 Found. C, 46 80; H, 7 73

Methyl 2-*O*-methyl-α-D-lyxofuranoside (0 15 g) was hydrolyzed in 0 1M sulfuric acid (2 ml) for 1 h, and the solution neutralized (barium carbonate) and evaporated to a syrup that crystallized Recrystallization from ethyl acetate provided 2-*O*-methyl-α-D-lyxose (0 11 g), m p 113–115°, $[\alpha]_D^{25}$ +3→−6° (*c* 0 6, water, constant value) Ganguly *et al* [23] reported m p 122° and $[\alpha]_D^{25}$ +6° for the naturally occurring L enantiomer

Anal Calc for $C_6H_{12}O_5$· C, 43 90, H, 7 37 Found. C, 43 70; H, 7 22

The 2- and 3-methyl ethers of methyl β-D-lyxofuranoside — Methylation of methyl 5-*O*-trityl-β-D-lyxofuranoside under conditions identical to those already described gave mainly methyl 2-*O*-methyl-5-*O*-trityl-β-D-lyxofuranoside, $[\alpha]_D^{25}$ −25° (*c* 1 2, chloroform)

Anal Calc for $C_{26}H_{28}O_5$: C, 74 26, H, 6 71 Found C, 73 77, H, 6 30.

Partial hydrolysis with aqueous acetic acid at 100° gave a mixture of 2- and 3-methyl ethers of methyl β-D-lyxofuranoside, $[\alpha]_D^{25}$ −45° (*c* 0 4, water), p m r data (D_2O, 70°) for the 2-methyl ethers δ 5 61, *J* 4 9 Hz (H-1), for the 3-methyl ether δ 5 47, *J* 4 7 Hz (H-1) ^{13}C N m r spectroscopy showed that one compound preponderated in a ratio of ~9·1, and this proved to be the 2-methyl ether, as 2-*O*-methyl-D-lyxose, m p and mixed m p 113–115° (from ethyl acetate), was obtained by acidic hydrolysis

Methyl 2-O-isopropyl-α,β-D-lyxofuranoside — 1,2·5,6-Di-*O*-isopropylidene-α-D-galactofuranose[21] (0.40 g) was shaken in 2-iodopropane (4 ml) and *N,N*-dimethylformamide (4 ml) containing silver oxide (4 ml) for 5 days Filtration and evaporation of the filtrate gave a syrup that was fractionated on a column of silicic acid (1 1 hexane–chloroform) to give 3-*O*-isopropyl-1,2 5,6-di-*O*-isopropylidene-α-D-galactofuranose (0 37 g), $[\alpha]_D^{25}$ −28° (*c* 1 3, chloroform)

Anal Calc for $C_{15}H_{26}O_6$. C, 59 58; H, 8 67 Found. C, 59 12; H, 8 54

The 3-isopropyl ether (0 27 g) was hydrolyzed in 0 1M sulfuric acid (5 ml) for 1 h at 100°, neutralized (barium carbonate), and evaporated to give a syrup that crystallized from ethyl acetate 3-*O*-Isopropyl-β-D-galactose (0 18 g) had m p 120–123°, $[\alpha]_D^{25}$ +85→+97° (*c* 0 4, water, constant value)

Anal Calc for $C_9H_{18}O_6$: C, 48.64, H, 8 16. Found: C, 48.25; H, 7 84.

Oxidation of 3-*O*-isopropyl-D-galactose with lead tetraacetate by the method

already described provided 2-*O*-isopropyl-D-lyxose (92% yield); $[\alpha]_D^{25}$ −5° (*c* 0 5, water).

Anal Calc for $C_8H_{16}O_5$: C, 49 99, H, 8 39 Found: C, 50 41, H, 8.12

2-*O*-Isopropyl-D-lyxose was converted into mixture of glycosides by treatment for 5 h in 0 5%, cold, methanolic hydrogen chloride The pyranosides were decomposed by successive treatment with sodium metaperiodate and barium hydroxide Purification was effected by column chromatography on silicic acid (eluant chloroform–methanol, 50.1 v/v) to provide methyl 2-*O*-isopropyl-α,β-D-lyxofuranosides, whose $[\alpha]_D^{25}$ value (+94°, *c* 0 2, water) indicated a predominance of the α anomer, p m r data (D_2O, 70°) δ_α 5 58, *J* 3 9 Hz (H-1), δ_β 5 56, *J* 4 7 Hz (H-1)

Anal Calc for $C_9H_{18}O_5$: C, 52 41, H, 8 80 Found. C, 51 94, H, 8 48.

The 3-^2H *and* 5-^2H *derivatives of methyl* α,β-D-*xylofuranoside* — D-Xylose-*3*-^2H and D-xylose-*5*-^2H were prepared as previously described[8]. The methyl furanosides were prepared by the method of Levene *et al* [24], p m r data for the 3-methyl ethers (D_2O, 70°) δ_β 5 37, *J* 1 2 Hz, δ_α 5 47, *J* 4 6 Hz (H-1)

Methyl 3-O-isopropyl-α,β-D-xylofuranoside. — 1,2 5,6-Di-*O*-isopropylidene-α-D-glucofuranose (5 0 g) was shaken for 3 days in 2-iodopropane (10 ml) and *N*,*N*-dimethylformamide (10 ml) containing silver oxide (10 g), and the mixture was diluted with dichloromethane, filtered, and the filtrate evaporated Reaction was not complete, and unchanged starting material crystallized from Skellysolve B. The remainder was partially hydrolyzed by the method described by Schmidt[25] for conversion of 1,2 5,6-di-*O*-isopropylidene-α-D-glucofuranose into 1,2-*O*-isopropylidene-α-D-glucofuranose The product was dissolved in ethyl acetate, which was extracted with water, and the organic layer was evaporated to give 3-*O*-isopropyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1.12 g), which from ether–Skellysolve B had m p. 83°, $[\alpha]_D^{25}$ −46° (*c* 0 4, chloroform)

Anal Calc for $C_{12}H_{22}O_6$. C, 54 94, H, 8 46 Found. C, 54.76, H, 8 73

A portion (0 56 g) was oxidized for 6 h in water (20 ml) containing sodium metaperiodate (1 0 g), and the solution was extracted twice with ethyl acetate The syrup (0 8 g) obtained on evaporation was reduced with sodium borohydride (0 20 g) in 30% aqueous methanol (20 ml) After 1 h, the solution was partially evaporated to remove methanol and the resulting aqueous solution was extracted with chloroform to give 3-*O*-isopropyl-1,2-*O*-isopropylidene-α-D-xylofuranose (0 36 g), $[\alpha]_D^{25}$ −50° (*c* 0 5, chloroform)

Anal. Calc for $C_{11}H_{20}O_5$: C, 56 88; H, 8 68 Found: C, 56 39, H, 8 21.

The 3-isopropyl ether (0 18 g) was hydrolyzed in 0 165M sulfuric acid (10 ml) for 2 h at 100° and the solution neutralized (barium carbonate), and evaporated to a syrup that crystallized Recrystallization for ether–ethyl acetate gave 3-*O*-isopropyl-α-D-xylose (101 mg), m p 113–114°, $[\alpha]_D^{25}$ +35° → +14° (*c* 0 3, water, constant value).

Anal. Calc for $C_8H_{16}O_5$: C, 49.99, H, 8 39. Found C, 49 75, H, 8 08

The pentose derivative was converted into a mixture of its methyl furanosides by the action of cold 0 5% hydrogen chloride in methanol for 3 h

(The foregoing series of reactions for preparation of the methyl glycosides was

repeated, except that sodium borodeuteride was used in place of sodium borohydride, so that methyl 3-*O*-isopropyl-α,β-D-xylofuranoside-5-^2H was the final product)

The methyl glycosides (130 mg) were fractionated on a column of silicic acid with 50 1 chloroform–methanol, as eluant, to give initially methyl 3-*O*-isopropyl-α-D-xylofuranoside (49 mg), $[\alpha]_D^{25}$ +140° (*c* 0 4, chloroform), p m r data (D_2O 70°) δ 5 47 *J* 4 3 Hz (H-1)

Anal Calc. for $C_9H_{18}O_5$ C, 52 41, H, 8 80 Found·C, 52 01, H, 8 69.

The second fraction consisted of methyl 3-*O*-isopropyl-β-D-xylofuranoside, $[\alpha]_D^{25}$ −79° (*c* 0 4, chloroform), p m r data (D_2O, 70°) δ 5 37 *J* 1 8 Hz (H-1)

Anal. Calc for $C_9H_{18}O_5$ C, 52 41, H, 8 80 Found C, 51 93, H, 8 90

Methyl 5-O-methyl α,β-D-galactofuranoside — Methyl 2,3-di-*O*-benzyl-6-*O*-trityl-α,β-D-galactofuranoside[26] (1 0 g) was methylated by the Kuhn procedure[27] and the product was partially hydrolyzed in 80% aqueous acetic acid (50 ml) for 15 min at 100° Evaporation gave a mixture that was fractionated on a column of silicic acid with 3 2 chloroform–hexane, as eluant to give methyl 2,3-di-*O*-benzyl-5-*O*-methyl-α,β-D-galactofuranoside (0 44 g)

Anal Calc for $C_{22}H_{28}O_6$. C, 68 02, H, 7 2 Found C, 67 56, H, 7 00

A portion of the product (0 20 g) was hydrogenolytically debenzylated in acetic acid containing 5% palladium on charcoal to give methyl 5-*O*-methyl-α,β-D-galactofuranoside (0 10 g); $[\alpha]_D^{25}$ −65° (*c* 0 5, water) As the rotation indicates, most of the product consisted of the β anomer

REFERENCES

1 D E Dorman, S J Angyal, and J D Roberts, *J Am Chem Soc*, 92 (1970) 1351–1354
2 A S Perlin, B Casu, and H J Koch, *Can J Chem*, 48 (1970) 2596–2606
3 P A J Gorin and M Mazurek, *Carbohydr Res*, 27 (1973) 325–339
4 P A J Gorin, *Carbohydr Res*, 39 (1975) 3–10
5 T Usui, N Yamaoka, K. Matsuda, K Tuzimura, H Sugiyama, and S Seto, *J Chem Soc*, (1973) 2425–2432
6 P A J Gorin, *Can J Chem*, 51 (1973) 2375–2383
7 P L Durette and D Horton, *Adv Carbohydr Chem Biochem*, 26 (1971) 49–125
8 P A J Gorin and M Mazurek, *Can J Chem*, 53 (1975) 1212–1223
9 H Spiesecke and W G Schneider, *J Chem Phys*, 35 (1961) 731–738
10 F J Weigert and J D Roberts, *J Am Chem Soc*, 89 (1967) 2967–2969
11 P A J. Gorin, *Can J Chem*, 52 (1974) 458–461
12 P A J Gorin, *Can J Chem*, 40 (1962) 275–282
13 P A. J Gorin and J F. T. Spencer, *Can J Chem*, 37 (1959) 499–502
14 M Karplus, *J Amer Chem Soc*, 85 (1963) 2870–2871
15 H J Koch and A S Perlin, *Carbohydr Res*, 15 (1970) 403–410
16 J Kenner and G N Richards, *J Chem Soc*, (1957) 3019–3024
17 C P J Glaudemans and H G Fletcher, Jr, *J Am Chem Soc*, 87 (1965) 4636–4641
18 M A Oldham and J Honeyman, *J Chem Soc*, (1946) 986–989
19 H B Woods, Jr, H W Diehl, and H G Fletcher, Jr, *J Am Chem Soc*, 78 (1956) 4715–4717
20 M Haga, M Takano, and S Tejima, *Carbohydr Res*, 21 (1972) 440–446
21 H Paulsen and H Behre, *Carbohyd Res*, 2 (1966) 80–81.
22 J Hildesheim, J Cleophax, and S D Gero, *Carbohydr Res*, 14 (1970) 305–314
23 A. K Ganguly, O Z Sarre, and J Morton, *J Chem. Soc D*, (1969) 1488–1489
24 P A Levene, A L Raymond, and R T Dillon, *J Biol Chem*, 95 (1932) 699–713

25 O. T. SCHMIDT, *Methods Carbohydr Chem*, 2 (1963) 318–325
26 H SAEKI AND T. IWASHIGE, *Chem Pharm Bull (Tokyo)*, 16 (1968) 1129–1132
27 R KUHN, H TRISCHMANN, AND I LÖW, *Angew Chem*, 67 (1955) 32
28 R G S RITCHIE, N CYR, B KORSCH, H J KOCH, AND A S. PERLIN, *Can J Chem*, 53 (1975) 1424–1433.
29 J F. PRESTON, III, AND J E GANDER, *Arch Biochem Biophys*, 124 (1968) 501–512