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THE 220 MHz PROTON MAGNETIC RESONANCE SPECTRA OF DERIVATIVES OF 5-DEOXY-5-IODO-α-D-*XYLO*-PENTOFURANOSE

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Abstract—The complete interpretation of the 220 MHz PMR spectra of two *xylo*-pentofuranoses has been achieved. The degree of magnetic non-equivalence of the C-5 methylene protons is strongly solvent-dependent. Some stereochemical conclusions are drawn from the measured coupling constants.

INTRODUCTION

AN INCREASING number of PMR spectra of carbohydrates are being reported of which the complete analysis has been achieved. Bhacca *et al.*,[1] with a pentopyranose (1-thio-α-L-arabinopyranose tetra-acetate), have demonstrated the value of studies at 220 MHz, in obtaining interpretable spectra. The complete interpretation of the spectra of two pentofuranoses (the 3-O-benzyl (**8**) and 3-O-*p*-nitrobenzyl (**6**) ethers of 5-deoxy-5-iodo-1, 2-O-isopropylidene-α-D-xylo-furanose) has now been made possible by this means. The findings constitute the starting point for studies of the more complex proton and fluorine magnetic resonance spectra, and as a prelude to X-ray structure analysis.

SPECTRA AND ASSIGNMENTS

3-O-Benzyl-5-deoxy-5-iodo-1,2-O isopropylidene-α-D-xylofuranose (**8**).

The 100 MHz spectrum of **8** in $CDCl_3$ (40 mg/0·35 ml; 34°) exhibited a singlet (τ 2·66; five protons) [aromatic protons]; a doublet (τ 5·92; one proton; splitting 3·1 Hz); a slightly irregular doublet (τ 6·68; two protons); two singlets (τ 8·50 and 8·69; each three protons) [isopropylidene groups]; and a complex region (τ 5·2–5·7; four protons), shown expanded in Fig 1.

Fig. 2 shows the central parts of the 220 MHz spectrum of **8** in $CDCl_3$ (148 mg/1·0 ml, 10°), together with the analysis. Data from the complete spectrum are given in Tables 1 and 2.

The doublet at low field (τ 4·07) is assigned to H-1 in the usual manner.[2] Since H-1 and H-2 have significantly different chemical shifts and H-2 and H-3 are weakly coupled (see below), the splitting is taken as the coupling constant $J_{1,2}$.[3]

The methylene protons H-6 and H-6′ are non-equivalent and give rise to a quartet which has been analysed as an AB spectrum.[4] The calculated parameters are given in the Tables.

The τ 5·39 doublet is assigned to H-2 because of the equality of the splitting with $J_{1,2}$ and by analogy with the assignment in the 220 MHz $CDCl_3$ spectrum of the *p*-nitrobenzyl analogue (**6**) which was made unequivocal on the basis of a spin decoupling experiment.

The 5·93 doublet is assigned to H-3, coupled to H-4. H-3 and H-2 have significantly

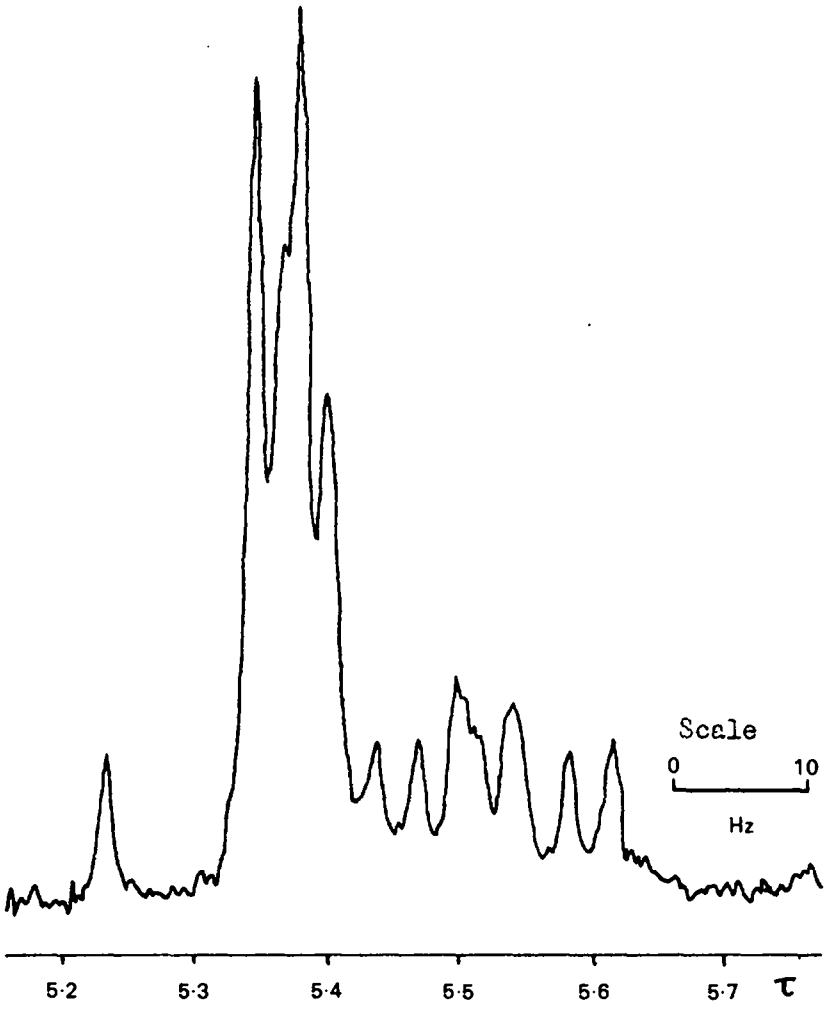
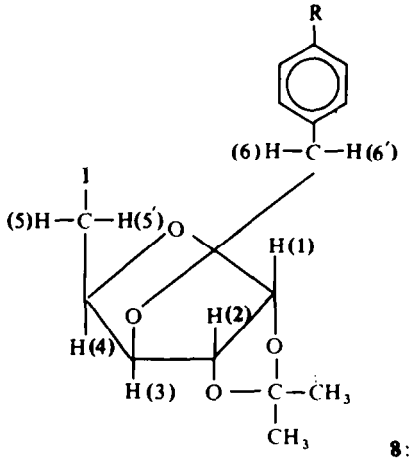


FIG 1. τ 5·2–5·7 Region of 100 MHz PMR spectrum of 3-*O*-benzyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose in $CDCl_3$.

different chemical shifts, so any fine splitting of the peaks of the H-2 doublet will measure directly the coupling constant $J_{2,3}$; thus $|J_{2,3}| \leqslant 0{\cdot}5$ Hz.

The methylene protons H-5 and H-5′ are non-equivalent and, with H-4, form an ABX system. Each X-peak is symmetrically split by coupling of H-4 with H-3 ($J_{4,3}$ = 3·1 Hz).

The full analysis of the H-4 multiplet is shown in Fig. 2. The AB part of the spectrum (τ 6·6–6·8) is "deceptively simple"[9]. Because of the superimposition of some lines and the possible very small intensities of others, it is difficult to pick out unequivocally the two constituent quartets which make up this AB part of the ABX spectrum, and a full analysis has not been attempted. However, both the X part (before the further splitting by H-3) and the AB part show strong resemblance to their corresponding



8: R = H
6: R = NO_2

parts in the "deceptively simple" ABX spectrum obtained by Abraham and Bernstein[5] for the ring protons of 2-furfurol at 60 MHz (see case b, p. 220 in Ref. 9). By analogy with previous results,[5] it may be said that both $\Delta\nu_{5,5'}$ and $\frac{1}{2}(J_{5,4} - J_{5',4})$ are small compared with $J_{5,5'}$.

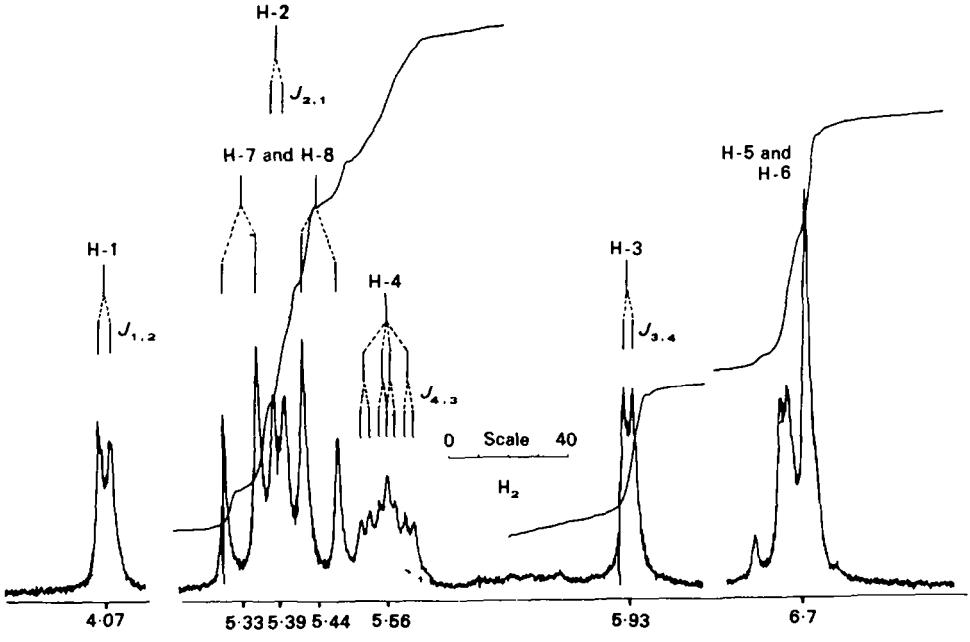


FIG 2. 220 MHz PMR spectrum of 3-*O*-benzyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose in $CDCl_3$; the aromatic and isopropylidene peaks are not shown.

* In discussing the spectra of **8** and **6**, H-6 has not been distinguished from H-6′, and H-5 has not been distinguished from H-5′; the assignments within each pair are arbitrary.

5-Deoxy-5-iodo-1,2,0-isopropylidene-3-0-p-nitrobenzyl-α-D-xylo furanose (**6**).

The 100 MHz spectrum of **6** in $CDCl_3$ was similar to the corresponding spectrum of **8**. The main difference was in the low field region where the aromatic protons of **6** appear as two doublets (τ 1·76 and 2·46; each two protons; splitting 8·0 Hz) arising from the superimposition of mutual splitting of two pairs of ortho-protons. The 5·0–5·8 region of the spectrum (four protons) was again complex.

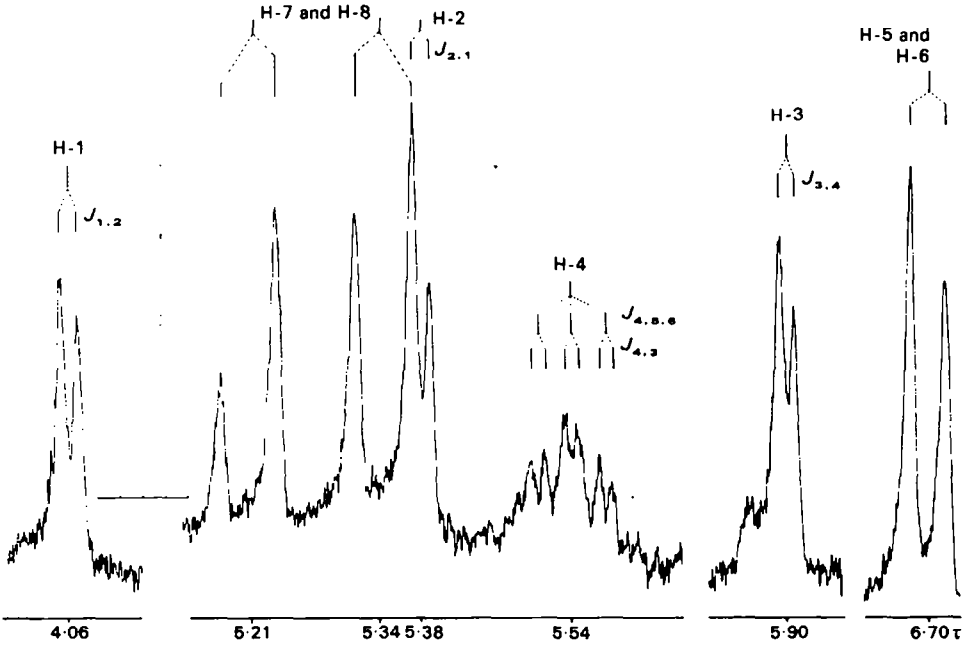


FIG 3. 220 MHz PMR spectrum of 5-deoxy-5-iodo-1,2-*O*-isopropylidene-3-*O*-*p*-nitrobenzyl-α-D-xylofuranose in $CDCl_3$; the aromatic and isopropylidene peaks are not shown.

Fig 3 shows the central parts of the 220 MHz spectrum of **6** in $CDCl_3$ (44 mg/1·0 ml; 40°), together with the analysis. (Tables 1 and 2.)

The τ 4·06 doublet is assigned to H-1, and the splitting taken as $J_{1,2}$, as for **1** above.

H-6 and H-6′ gives rise to an AB quartet, one of the peaks from which overlaps with half of the doublet centred at τ 5·38. Calculated[4] parameters for H-6 and H-6′ system are given in the Tables.

The doublets centred at τ 5·38 and τ 5·90 both have splittings equal, within the errors of measurement, to the coupling constant $J_{1,2}$. The assignment of the τ 5·38 doublet to H-2 was made on the basis of a frequency-sweep spin-decoupling experiment: when the H-1 doublet was irradiated with a decoupling radiofrequency, the τ 5·38 doublet collapsed to a singlet and the τ 5·90 doublet remained unaltered.

The τ 5·90 doublet is then assigned to H-3, coupled to H-4 ($J_{3,4} = 3·3$ Hz). As in the case of the benzyl-analogue (**8**), $|J_{2,3}| \leqslant 0·5$ Hz. In $CHCl_3$, the methylene protons H-5 and H-5′ are apparently equivalent and they give rise to a simple doublet (centred at 6·70).

As before, this may be compared to the AB part of the "deceptively simple" ABX

TABLE 1. CHEMICAL SHIFTS (τ-VALUES) PPM (220 MHz)

Compd.	Solvent	Aromatic	H-1	H-2	H-3	H-4	(H-5	H-5')	(H-6	H-6')	Isopropylidene
8	$CDCl_3$	2·7*	4·07	5·39	5·93	5·56	6·70*	6·70*	5·33	5·44†	8·50, 8·68
6	$CDCl_3$	1·82, 2·51	4·06	5·38	5·90	5·54	6·70	6·70	5·21	5·34†	8·50, 8·69
6	CD_3CO CD_3	1·77, 2·31	4·08	5·13	5·88	5·57	6·59	6·65†	5·03	5·24†	8·55, 8·71

* Approximate value
† Not necessarily respectively

TABLE 2. COUPLING CONSTANTS AND CHEMICAL SHIFT DIFFERENCES (Hz)

Compd.	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,5'}$	$J_{6,6'}$	$J_{6,6'}$
8	$CDCl_3$	4·1	0·5	3·1	N.D.	N.D.	N.D.	N.D.	11·2	24·4
6	$CDCl_3$	3·7	0·5	3·3	7·4	7·4	N.D.	0	12·3	27·3
6	CD_3CO CD_3	4·0	0·5	3·2	7·5 and	6·5†	9	14	12·9	47·1

N.D. = not determined
† not necessarily respectively

spectrum[5] for the ring protons of 2-furfurol. For this simplification of the normal ABX spectrum to occur, the following conditions must be satisfied.

$$\Delta\nu_{5,5'} \to 0$$

$$\tfrac{1}{2}(J_{5,4} - J_{5',4})/J_{5,5'} \to 0$$

Thus H-5 and H-5′ have nearly identical chemical shifts (at τ 6·70) and are equally or almost equally coupled to H-4.

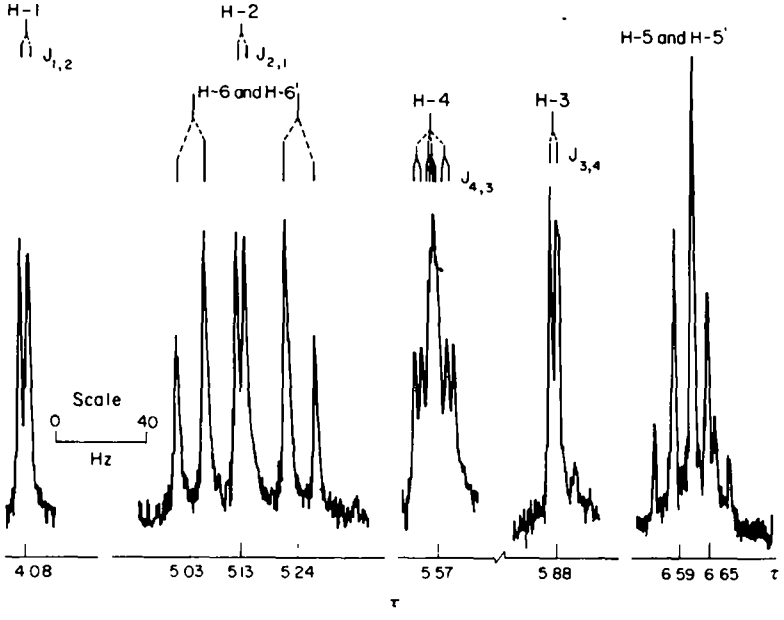


FIG 4. 220 MHz PMR spectrum of 5-deoxy-5-iodo-1,2-O-isopropylidene-3-O-*p*-nitrobenzyl-α-D-xylofuranose in $CD_3.CO.CD_3$; the aromatic and isopropylidene peaks are not shown.

Fig 4 shows the central parts of the 220 MHz spectrum of **6** in CD_3 CO CD_3 (44 mg/1·0 ml; 40°), together with the analysis. Data from the complete spectrum are given in the Tables.

This spectrum is similar to the 220 MHz $CDCl_3$ spectrum, but there are two significant differences. First, a down-field solvent shift of H-2 has taken place, removing the overlap of two peaks which occurred in the $CDCl_3$ spectrum, showing clearly the τ 5·0–5·3 region to be a doublet and a separate quartet. Secondly, in $CD_3CO.CD_3$ the methylene protons H-5 and H-5′ are observably non-equivalent, giving rise with H-4 to an ABX spectrum in which each X-peak is symmetrically split by coupling with H-3. There is some overlapping in the AB part of the pattern, but the two constituent quartets can be distinguished. The coupling constant and chemical shifts of the system can therefore be calculated.[6] The following values, taken from the observed

spectrum have been used for the calculations:

$$|J_{5,5'}| = 9 \text{ Hz}$$
$$|2D_+| = 17 \text{ Hz}$$
$$|2D_-| = 16 \text{ Hz}$$
$$|J_{5,4} + J_{5',4}| = 14 \text{ Hz}$$

The results of the calculations are given in the Tables.

DISCUSSION

Comparison of the τ 5·2–5·7 regions in the 100 MHz (Fig. 1) and 220 MHz (Fig 2) spectra of 3-O-benzyl-5-deoxy-5-iodo-1,2-O-isopropylidene-α-xylofuranose (**8**) in $CDCl_3$ demonstrates forcibly the advantages of obtaining the PMR spectra of carbohydrates at as high a magnetic field as available. In this region of the 100 MHz spectrum no patterns characteristic of particular groupings of protons can be distinguished; in the 220 MHz spectrum the pattern of each multiplet indicates the coupling characteristics of the protons involved.

Inspection of Table 2 shows that the degree of magnetic non-equivalence (measured by $\Delta\nu_{5,5'}$ and $\Delta\nu_{6,6'}$) of the two sets of methylene protons, H-5 and H-5′, and H-6 and H-6′, in **6** is solvent dependent, but in the absence of further information (e.g. from spectra at different temperatures) it is not possible to decide the origin of this non-equivalence.[7,8]

The values of H-1 in **8** and **6** (Table 1) show good agreement with published values (4·07 ± 0·1 ppm) for 1,2,-O-isopropylidene-α-D-xylohexofuranose derivatives.[9] The general shape of the furanose ring in **8** and **6** would appear to be similar to that in compounds studied by Abraham *et al.*[9] No attempt is made here to determine the exact stereochemistry of the ring by substitution of the measured coupling constants into the Karplus[10] equation. However, the comparable values of $J_{1,2}$ and $J_{3,4}$, and the weak or vanishing coupling between H-2 and H-3, in **8** and **6**, imply that these compounds exist in the "skew" conformation in which C-2 and C-3 are displaced equally and in opposite senses from the plane of the other ring atoms such that the dihedral angle between H-2 and H-3 approaches 90°.

EXPERIMENTAL

NMR spectra. The 100 MHz spectra were recorded on a Perkin–Elmer Spectrometer, and the 220 MHz spectra on a Varian HR220 spectrometer. The pentoses were examined as solns in $CDCl_3$ or perdeuteroacetone at the concentrations and temps indicated. TMS was used as internal reference. The spin-decoupling experiment was performed at 60 MHz on a Perkin–Elmer R.10 spectrometer.

Thin layer chromatography was carried out using the following systems: coating 1, Kieselgel $HF_{254+366}$; coating 2, Kieselgel PF_{254}. Solvent A, benzene : ethyl acetate (3 : 7 v/v); solvent B, chloroform : light petroleum (1 : 1); solvent C, chloroform : light petroleum (1 : 2); solvent D, chloroform; solvent E, chloroform : light petroleum (2 : 1).

1,2-O-*Isopropylidene*-α-D-*xylofuranose* (**1**). This compound, synthesized by the method Levene and Raymond,[2] had b.p. 144° (0·1 mm); $[\alpha]_D^{18}$ −19·0° (*c* 3·4 H_2O) Lit.[2] $[\alpha]_D^{22}$ −19·9° (H_2O).

1,2-O-*Isopropylidene*-5-O-*methane sulphonyl*-α-D-*xylofuranose* (**2**), was synthesized by a modification of the method of Helferich and Burgdorp.[3] Freshly distilled methanesulphonyl chloride (8·5 ml) was added dropwise to soln of the isopropylidine derivative (I, 19g) in dry pyridine (100 ml) at − 10°. After 1 hr at 0°,

water (12 ml) was added stepwise at 5 min intervals. After a further 15 min, the mixture was passed into ice-water (400 ml) and the product was extracted with $CHCl_3$. The organic soln washed with water and dried ($MgSO_4$) was evaporated to a viscous syrup. To this toluene (100 ml) was added and the solvent together with residual pyridine was removed under reduced press at 40°. Repetition of this distillation procedure, 5 times, gave a pyridine-free product, which was crystallized from hexane-EtOAc (2:3 v/v). The methanesulphonate (**2**) had m.p. 139°, $[\alpha]_D^{25}$ − 23·1 (*c* 2·6 MeOH), yield, 25g, 93%. (Found: C, 40·5; H, 5·9; S, 12·0 Calc for $C_9H_{18}O_7S$; C, 40·3 H, 6·0; S, 12·0%), Lit.[3] m.p. 129°, 133° $[\alpha]_D^{20}$ − 21·2° (MeOH). The PMR spectrum of **2** at 100 MH, in CH_3SOCD_3 exhibited a doublet at τ 4·11 (one proton), J = 3·4 Hz, (anomeric proton), doublet τ 4·51 (one proton), J = 5 Hz, which vanished on exchange with D_2O (hydroxyl proton), an unresolved complex region τ 5·5–6·0 (five protons H-2; H-4, and H-5) singlet τ 6·8 (CH_3 protons, methane sulphonyl group), an unresolved complex, τ 7·5 ($CD_3SO_2CD_3$) and two singlets τ 8·6 and τ 8·75 (3 protons in each, isopropylidene CH_3 groups). The IR spectrum showed bands consistent with the proposed structure.

3-O-*Acetyl*-1,2-O-*isopropylidine*-5-O-*methane sulphonyl*-α-D-*xylofruranose* (**3**). Acetylation of **2** with Ac_2O (2 moles) in dry pyridine under the conditions described gave the 3-0 *acetate* (**3**) which after recrystallization from hexane-EtOAc had m.p. 105–106°, $[\alpha]_D^{20}$ −9·5 (*c* 1·7 MeOH). [Found C, 41·8; H, 5·8; S, 10·5; $C_{11}H_{18}O_8S$ requires: C, 42·6, H, 5·8; S, 10·3%]. The PMR spectrum at 100 MHz in $CDCl_3$ exhibited the following bands: A doublet at τ 4·06 (one proton) J = 3·5 Hz (anomeric proton), a doublet τ 4·73 (one proton), J = 3 Hz (H-3 proton), an unresolved complex region τ 5·4–5·7 (4 protons, H-2, H-3 and H-5) a singlet τ 6·9 (3 protons, methyl CH_3), singlet τ 7·88 (3 protons; acetate-CH_3), two singlets τ 8·47 and τ 8·67 (3 protons under each). The IR spectrum showed bands at 1742 (CO), 1376, 1357, and 1179, 1170 ($-SO_2$) cm^{-1}.

1,2-O-*Isopropylidene*-5-*toluene*-p-*sulphonyl*-α-D-*xylofuranose* (**4**). This compound was prepared from the isopropylidene **2** by the method of Tipson.[13] Improved yields were obtained by evaporation of the dried chloroform extract of the product at 50° (under reduced press) to remove the majority of the remaining pyridine. The resulting syrup, taken up in CH_2Cl_2 was washed with H_2SO_4 aq, sat $NaHCO_3$aq and water as described. The tosylate (**4**) had m.p. 133–134°, $[\alpha]_D^{26}$ − 13·6° (*c* 1·5 in $CHCl_3$) [Found: C, 51·8; H, 6·3; S, 9·4 Calc. for $C_{15}H_{20}O_7S$; C, 52·3; H, 5·9; S, 9·3%], Lit.[13] m.p. 133–134° $[\alpha]_D^{20}$ − 13·0 (*c* 2·0 in $CHCl_3$). The PMR spectrum at 100 MHz in $CDCl_3$ exhibited two doublets τ 2·21 and 2·75 (2 protons in each), J = 8 Hz (aromatic protons), a doublet τ 4·14 (one proton), J = 3·5 Hz (anomeric proton) an unresolved complex region τ 5·50–5 95 (5 protons, H-3, H-4, H-5), a doublet τ 7·4 (one proton), J = 5·5 Hz, this doublet vanished on exchange with D_2O (hydroxyl proton), a singlet τ 7·56 (3 protons) (toluene CH_3 protons), two singlets τ 8·55–8·71 (3 protons each); isopropylidine group) Lit[14] NMR ($CDCl_3$) τ 4·12 (H-1 doublet) 1·24 Hz. The yields of the tosylate obtained by this method were between 72 and 92%.

1,2-*Isopropylidene*-3-0-p-*nitrobenzyl*-5-0-*toluene*-p-*sulphonyl*-α-D-*xylofuranose* (**5**). *p*-Nitrobenzyl bromide (3·24 g, 15 mmoles, recryst from EtOH) and dry Ag_2O (1·5 g) was added to a soln of **4** (3·44 g, 10 mmoles) in dry DMF (15 ml). The mixture was shaken in the dark, at room temp. After 24 hr more dry Ag_2O (1·5 g) was added. After a further 24 hr, the mixture was diluted with EtOAc (150 ml), filtered and the organic soln was washed with water (3 × 100 ml), dried ($MgSO_4$). Removal of the solvent gave a syrup which by TLC (coating 1, solvent B) on triple elution showed at least 7 components. The principal product (*Rf* 0·4 was separated by preparative layer chromatography in solvent E (three elutions), giving *p*-nitrobenzyl ether (**5**) as a syrup which after recrystallization from EtOH, has m.p. 110–111° $[\alpha]_D^{26}$ − 24·2° (*c* 1·5 in $CHCl_3$). [Found: C, 54·9; H, 5·2; N, 2·8; S, 6·9. $C_{22}H_{25}NO_9S$ requires: C, 55·1; H, 5·3; N, 2·9; S, 6·7%]. The PMR spectrum at 100 MHz, in $CDCl_3$, exhibited four doublets τ 1·84, 2·24, 2·58, 2·70 (2 protons in each *doublet*), J = 8 Hz (aromatic protons), a doublet τ 4·13 (one proton), J = 4 Hz (aromatic proton), an unresolved complex region τ 5·1–5·9 (6 protons) and doublet τ 6·00 (one proton), J = 2·5 Hz (H-2, H-3, H-5 and *p*-nitrobenzyl —CH_2-protons), a singlet τ 7·58 (3 protons) (toluene CH_3 protons), two singlets τ 8·54 and 8·69 (3 protons in each) (isopropylidene group).

5-*Deoxy*-5-*iodo*-1,2-O-*isopropylidene*-3-0-p-*nitrobenzyl*-α-D-*xylofuranose* (**6**). The tosylate **5** (0·5g) and NaI (0·5 g) dissolved in acetone (5 ml) were heated at 100° for 24 hr. The cooled soln was poured into water (50 ml) and the product was extracted with CH_2Cl_2 (50 ml × 3). Evaporation of the solvent gave a syrup homogeneous on TLC (coating 2, solvent C, 4 times development) *Rf* 0·45. Crystallization from EtOH give the 5-*deoxy*-5-*iodo* derivatives (**10**) yield (62%, 0·27g), m.p. 100°, $[\alpha]_D^{23}$ − 80·3° (*c* 0·6 in $CHCl_3$). [Found: C, 41·8; H, 4·0; I, 29·2; N, 3·2 $C_{15}H_{18}INO_6$ requires: C, 41·4 H, 4·2; I, 29·2; N, 3·2%].

3-0-*Benzyl*-1,2-0-*isopropylidene*-5-0-*toluene*-p-*sulphonyl*-α-D-*xylofuranose* (**7**). Redistilled benzyl bromide (1·78 ml, 15 mmoles) and Ag_2O (2 g) were added to soln of **4**, 0·44 g, 10 mmoles) in dry DMF (20 ml), as

in the preceding experiment. The preparative chromatographic separation in solvent D (one elution), gave the *benzyl ether* (7) *Rf* 0·4 as a syrup (1·34 g, 31%) $[\alpha]_D^{21}$ −29·0 (*c* 1·30 in $CHCl_3$). [Found: C, 60·5; H, 6·2; S, 7·8; $C_{22}H_{26}O_7S$ requires: C, 60·8; H, 6·0; S, 7·3%]. The PMR spectrum at 100 MHz in $CDCl_3$ exhibited a doublet τ 2·25 (2 protons), J = 8 Hz and a complex region τ 2·6–2·9 (7 aromatic protons), a doublet, τ 4·17 (one proton), J = 3·7 Hz (anomeric proton) and a further complex region τ 5·2 – 5·6 (6 protons) and a doublet τ 6·60 (one proton), J = 2·8 Hz (H-2, H-3, H-4, H-5 and benzyl —CH_2-protons), a singlet τ 7·61 (3 protons) (toluene CH_3 protons) and two singlets τ 8·58 and 8·73 (3 protons each) (isopropylidene group).

3-O-*Benzyl*-5-*deoxy*-5-*iodo*-1,2-*isopropylidene*-α-D-*xylofuranose* (**8**). The tosylate **7** (1·55 g) and NaI (1·5 g) were heated in acetone (10 ml) in a sealed tube at 100° for 24 hr and the product was isolated as described for **6**. The benzyl iodosugar (**8**) was obtained colourless needles (1·33 g, 93%), recrystallized from EtOH, m.p. 74–75°; $[\alpha]_D^{23}$ − 81·5° (*c* 0·68 in $CHCl_3$). [Found: C, 46·2; H, 4·8; I, 32·7. $C_{15}H_{19}IO_4$ requires: C, 46·5; H, 4·9; I, 32·5%].

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