CHARACTERISATION OF METHYL DERIVATIVES OF D-GALACTOPYRANOSE AND METHYL ETHERS OF GALACTITOL BY P.M.R. SPECTROSCOPY*

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ABSTRACT

The 60- and 100-MHz p.m.r. spectra of methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranoside (**1**) and methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside (**2**) (dissolved in benzene, deuterium oxide, and other solvents) have been analysed for their methoxyl and anomeric proton signals, and compared with the spectra of the corresponding D-glucose derivatives, namely, methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (**3**) and methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**4**). The spectrum of a mixture of 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranose (**5**) and 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranose (**6**) was obtained similarly, and the signals for all eight methoxyl groups were assigned for solutions in benzene and deuterium oxide. The spectra of 2,3,4,6-tetra-*O*-methyl-D-galactitol (**7**) and hexa-*O*-methylgalactitol (**8**) were analysed for their methoxyl-group signals in six solvents; these were assigned by using derivatives of **7** and **8** in which CH_3O groups were replaced by CD_3O groups to different extents. Compared with the use of the spectra of **1** and **2**, the use of the p.m.r. spectrum of **7** (dissolved in benzene) was found to be a relatively simple method for identification of an unknown methyl ether of D-galactopyranose. The dependence of the spectra of the D-galactose derivatives (**1**, **2**, **5**, **6**, **7** and **8**) on concentration was measured for benzene solutions at 60 MHz; the spectra of these compounds in the other solvents used showed negligible dependence on concentration.

INTRODUCTION

The p.m.r. spectra of solutions of partially and fully methylated D-galactopyranose[1,2], including the mono-methylated derivatives[3], in deuterium oxide had been determined. These spectra, together with those of methyl ethers of methyl D-galactopyranosides[2] and of galactitol[2,4] have been studied as a means of deter-

*Dedicated to Dr. Nelson K. Richtmyer in honour of his 70th birthday.

mining their structures. The positions of methoxyl substitution in certain of the partially methylated compounds could not be deduced from such spectra without reference to the spectra of authentic specimens[1,2], because neighbouring groups (hydroxyl or methoxyl) influence in different ways the chemical shifts of the methoxyl groups (*cf.* Ref. 3). In order to identify a partially or fully methylated derivative of D-galactopyranose, the compound is converted into the per(deuteriomethyl)ated methyl glycosides, and the chemical shifts for methoxyl in the p.m.r. spectrum of a solution in benzene are compared with those assigned to the methoxyl signals of methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranoside (**1**) and methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside[5] (**2**). A similar procedure has been described by Gagnaire and Odier[6] for assigning methoxyl signals in the p.m.r. spectra of methyl ethers of methyl D-glucopyranosides. An extension of this procedure would then consist in using the p.m.r. spectra of 2,3,4,6-tetra-*O*-methyl-D-galactopyranose (**5**+**6**) and 2,3,4,6-tetra-*O*-methyl-D-galactitol (**7**) as a means of identifying methyl ethers of D-galactopyranose.

RESULTS AND DISCUSSION

*P.m.r. spectra of methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactopyranoside* (**1**) *and methyl 2,3,4,6-tetra-*O*-methyl-β-D-galactopyranoside* (**2**). — The p.m.r. spectra of both **1** and **2** (in benzene) have now been determined at 100 MHz, and they confirm the assignments made[5] at 60 MHz. The chemical shifts of the methoxyl groups in the p.m.r. spectra of **1** and **2** (in benzene) were found to be dependent on the concentration of the solution, as shown in Fig. 1; it is, however, clear that the order in which the

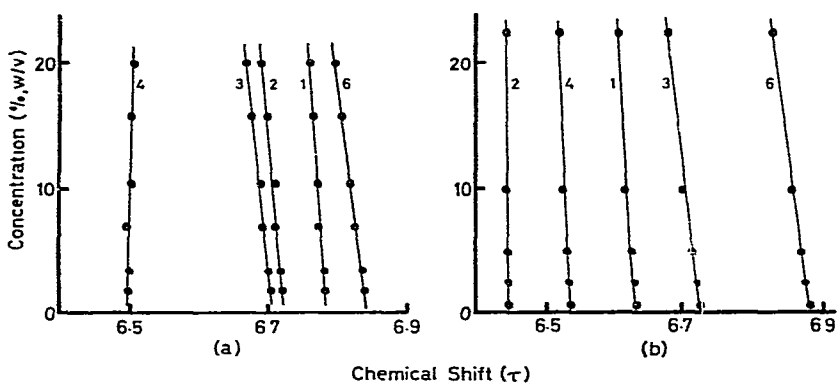

Fig. 1. Concentration-dependence of methoxyl chemical-shifts (numbered 1, 2, 3, 4, and 6) in the p.m.r. spectra (60 MHz) of (a) compound **1**, and (b) compound **2**, in benzene at 26°.

methoxyl signals appear (and, consequently, the assignments made for them in the spectra of **1** and **2**) is not affected within the range of concentrations used (up to 22%, w/v). Except for the low-field 4-methoxyl group of **1**, all the methoxyl groups absorb at higher field as the benzene:solute ratio is increased. In the spectrum of **2**, the

2-methoxyl group, appearing at lowest field, is least affected by dilution. The methoxyl signals of the D-glucose derivatives methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (**3**) and methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (**4**) showed similar concentration-dependence in benzene, the low-field signals being affected least by a change in concentration.

Table I lists, for the methoxyl groups and the anomeric protons, the chemical shifts found for the p.m.r. spectra of **1** and **2** in six solvents. These signals showed negligible concentration-dependence in solvents other than benzene*.

TABLE I

P.M.R. PARAMETERS[a] FOR COMPOUNDS **1–4**

Compound	*Solvent*	*H-1*		*Chemical shift of OMe group on carbon atom*				
		$\tau(\tau')$	$J_{1,2}$(Hz)[b]	*1*	*2*	*3*	*4*	*6*
1	C_6H_6	5.21	3.2	6.77	6.71	6.69	6.50	6.82
	CCl_4	5.39	2.8	6.68	6.59	6.56	6.55	6.69
	Δ[c]	−0.18		0.09	0.12	0.13	−0.05	0.13
2	C_6H_6	5.87	7.3	6.61	6.44	6.70	6.52	6.85
	CCl_4	6.05	7.0	6.585	6.54	6.55	6.54	6.68
	Δ[c]	−0.18		0.025	−0.10	0.15	−0.02	0.17
3[d]	C_6H_6	5.32	3.4	6.81	6.77	6.41	6.50	6.77
4[d]	C_6H_6	5.95	6.7	6.64	6.46	6.41	6.55	6.76
1	$CDCl_3$	5.14	3.3	6.59	6.49	6.49	6.44	6.60
	CH_2Cl_2	5.22	3.0	6.65	6.58	6.545	6.51	6.65
	D_2O	5.00	2.8	6.62	6.58	6.54	6.51	6.60
	$HCONMe_2$	5.21	2.6	6.69	6.63	6.57	6.54	6.68
2	$CDCl_3$	5.855	7.0	6.50	6.43	6.48	6.445	6.60
	CH_2Cl_2	5.91	7.5	6.55	6.505	6.53	6.505	6.65
	D_2O	5.68	7.5	6.46	6.47	6.50	6.50	6.59
	$HCONMe_2$	5.885	7.4	6.585	6.55	6.55	6.53	6.67

[a]Chemical shifts are relative to internal sodium 4,4-dimethyl-4-silapentanesulphonate for solutions in deuterium oxide (τ' scale[1]) and relative to internal tetramethylsilane for the other solutions (τ scale). Shifts in benzene are for 10% solutions at 26° determined at 60 MHz. Shifts in all other solutions are at 32° and 100 MHz. [b]Observed spacings of the doublets. [c]$\Delta = \tau_{C_6H_6} - \tau_{CCl_4}$(p.p.m.). [d]Assignments for methoxyl groups taken from Ref. 6; parameters given here are from spectra redetermined for 10% solutions at 26° (see Experimental section).

On considering the influence of benzene on the chemical shifts of methoxyl for **1** and **2** (see Table I), it was found that differences in anisotropic effect (Δ) upon anomeric change (α to β) are only significant for C-2 (−0.22 p.p.m.) and C-1 (−0.065 p.p.m.), just as, in all solvents, the 2- and 1-methoxyl chemical-shifts are most

*There appears to be a link between the change in methoxyl chemical-shifts with concentration in benzene (Fig. 1, a and b) and the anisotropic effect (Δ, Table I).

influenced by anomeric change. The anisotropic effect of benzene, particularly, enhances the effect, on the p.m.r. signal of the 2-methoxyl group, produced by anomeric change. For H-1, the anisotropic effect is the same for both anomers, whereas it is well known that the chemical shifts differ. These results can be understood on the assumption that there is a different favoured orientation of benzene[7] with respect to the atoms in the vicinity of C-1 (the most electron-deficient carbon atom in the sugar derivative) for the two anomeric forms.

Comparison of the p.m.r. parameters of **1** and **2** in benzene with those of the corresponding D-glucoside derivatives (**3** and **4**) (10% solutions in benzene, at 26°) leads to the following conclusions (see Table II). (*i*) On comparing the spectrum of the

TABLE II

CHANGE IN CHEMICAL SHIFT[a] (p.p.m.) OF METHOXYL PROTONS ON CHANGING

(a) FROM METHYL 2,3,4,6-TETRA-*O*-METHYL-α-D-GALACTOPYRANOSIDE AND -GLUCOPYRANOSIDE TO METHYL 2,3,4,6-TETRA-*O*-METHYL-β-D-GALACTOPYRANOSIDE AND -GLUCOPYRANOSIDE;

(b) FROM METHYL 2,3,4,6-TETRA-*O*-METHYL-α- AND -β-D-GALACTOPYRANOSIDE TO METHYL 2,3,4,6-TETRA-*O*-METHYL-α- AND -β-D-GLUCOPYRANOSIDE, RESPECTIVELY

	Δ(1-OMe)	*Δ(2-OMe)*	*Δ(3-OMe)*	*Δ(4-OMe)*	*Δ(6-OMe)*
(a)	*α→β*	*(change at C-1, ax OMe→ eq OMe)*			
Gal	−0.16	−0.27	0.01	0.02	0.03
G	−0.17	−0.31	0	0.05	−0.01
(b)	*Gal→G*	*(change at C-4, ax OMe→eq OMe)*			
α	0.04	0.06	−0.28	0	−0.05
β	0.03	0.02	−0.29	0.03	−0.09

[a]Determined at 60 MHz for 10% solutions in benzene at 26°.

α with that of the β anomer, it is seen that the change in methoxyl chemical-shift is of similar magnitude for corresponding methoxyl groups in the derivatives both of D-galactose and D-glucose (see Table IIa), the change decreasing in the following order: 2-methoxyl > 1-methoxyl > 4-methoxyl ≃ 6-methoxyl ≃ 3-methoxyl ≃ 0. (*ii*) On comparing the spectra of the derivatives of D-galactose (**1** and **2**) with those of D-glucose (**3** and **4**), it is seen that the change in methoxyl chemical-shift is of similar magnitude, and in the same direction, for corresponding methoxyl groups in the α- and β-D-glycosides, the 3-methoxyl groups being affected the most (see Table IIb). (*iii*) The effect of a change of configuration at C-1 and C-4 (an axially attached methoxyl group being converted into an equatorially attached in both cases) produces a similar downfield shift of ~0.29 p.p.m. of the signals for neighbouring, equatorial methoxyl groups (2-methoxyl group in Table IIa, and 3-methoxyl group in Table IIb). In contrast, the methoxyl group that is actually involved in the structural change is less affected: the change at the anomeric centre produces in the 1-methoxyl chemical-shift

a decrease of 0.16 p.p.m. (see Table IIa), and the 4-methoxyl is not significantly affected (see Table IIb).

P.m.r. spectra of 2,3,4,6-tetra-O-methyl-α-D-galactopyranose (**5**) *and 2,3,4,6-tetra-O-methyl-β-D-galactopyranose* (**6**). — The p.m.r. spectrum of an equilibrated mixture of **5** and **6** in benzene at both 60 and 100 MHz shows, at certain concentrations, eight distinct lines for the eight methoxyl groups; assignments are indicated in Fig. 2.

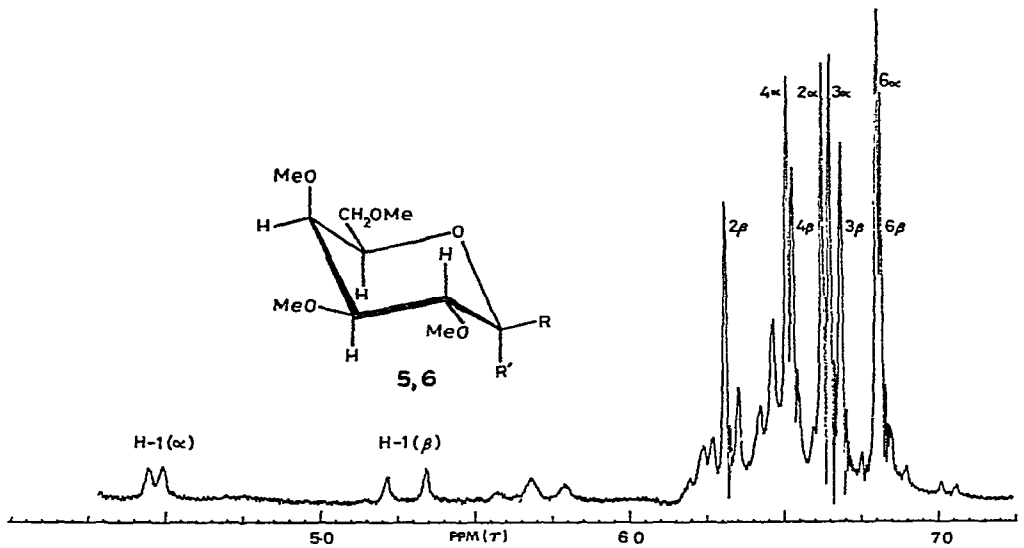

Fig. 2. P.m.r. spectrum (60 MHz) of an equilibrated mixture of **5** (R = H, R′ = OH) and **6** (R = OH, R′ = H) in benzene [15% (w/v)] at 26°. [Under these conditions, the methoxyl signals have the following chemical shifts (τ) for the order in which they appear in the spectrum (*cf.* Table III): 6.31 (2β), 6.51 (4α), 6.53 (4β), 6.62 (2α), 6.65 (3α), 6.685 (3β), 6.80 (6α) and 6.81 (6β)].

As is shown in Fig. 3, the concentration-dependence of **5** and **6** in benzene is much greater than that of compounds **1** and **2**, especially for dilute solutions (<5%, w/v). For **5** and **6** in deuterium oxide, there was a change in chemical shift of no more than 0.005 p.p.m. when the solution was diluted 2.5 times.

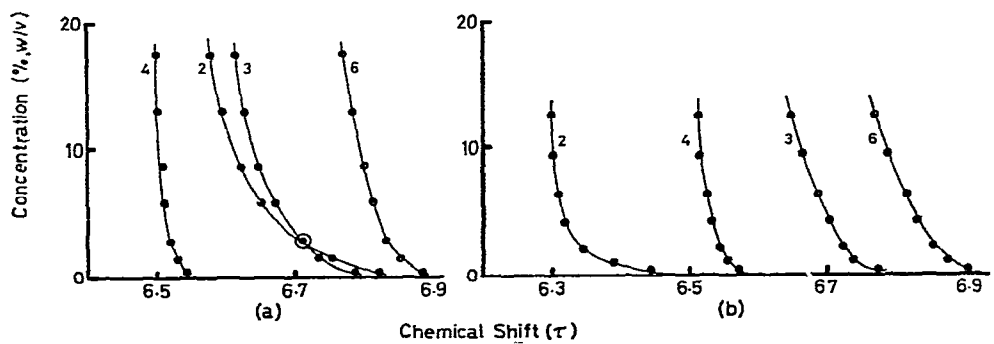

Fig. 3. Concentration-dependence of methoxyl chemical-shifts (numbered 2,3,4, and 6) in the p.m.r. spectra (60 MHz) of (a) compound **5**, and (b) compound **6**, in benzene at 26°.

By recording the p.m.r. spectra of a large number of partially methylated derivatives of D-galactose in deuterium oxide, we have confirmed[2] that methoxyl chemical-shifts cannot be assigned unless the spectrum of the methyl ether is compared with that of an authentic sample. On the other hand, identification of the partially methylated compound is possible by converting it into its methyl glycosides, (deuteriomethyl)ating as described earlier[5], hydrolysing the glycosidic mixture, and comparing the p.m.r. spectrum of the resultant compound in benzene with the spectrum of (**5**+**6**) at the same concentration and temperature. Any methoxyl signals absent from the spectrum correspond to hydroxyl groups in the D-galactopyranose methyl ether. Compared with the method of using the spectra of the methyl glycosides (**1** and **2**) for identification, this method has the disadvantage that the methoxyl signals studied are much more concentration-dependent. The spectrum of the pair of (deuteriomethyl)-ated D-galactose methyl ethers (α and β anomers) does, however, show a maximum of eight methoxyl signals, as opposed to the ten of the methyl D-galactosides.

The 100-MHz spectra of (**5**+**6**) in deuterium oxide, dichloromethane, and carbon tetrachloride were also recorded. Those obtained with the last two solvents were unsatisfactory, as very poor separation of the methoxyl signals was observed. Only the p.m.r. parameters obtained from the spectra of these compounds in benzene and deuterium oxide are presented in Table III.

TABLE III

P.M.R. PARAMETERS[a] FOR COMPOUNDS **5** AND **6**

Compound	*Solvent*	*H-1*		*Chemical shift of OMe group on carbon atom*			
		$\tau(\tau')$	$J_{1,2}$(*Hz*)[b]	*2*	*3*	*4*	*6*
5	C_6H_6	4.48	2.8	6.61	6.64	6.51	6.79
	D_2O	4.58	3.6	6.58	6.53	6.51	6.63
6	C_6H_6	5.29	7.4	6.30	6.66	6.52	6.78
	D_2O	5.35	7.5	6.45	6.512	6.508	6.62

[a]Chemical shifts in benzene are those determined from Fig. 3 for 10% solutions at 26° relative to tetramethylsilane (τ scale, 60 MHz); for solutions in deuterium oxide, relative to sodium 4,4-dimethyl-4-silapentanesulphonate (τ' scale[1], 100 MHz). [b]Observed spacings of the doublets. [c]For a 15% solution in benzene of a mixture of compounds **5** and **6**, the relative positions of the 6-methoxyl signals are reversed, as shown in Fig. 2.

*P.m.r. spectra of 2,3,4,6-tetra-*O*-methyl-*D*-galactitol* (**7**). — Reduction of 2,3,4,6-tetra-*O*-methyl-D-galactose with sodium borohydride yields **7**; the 60-MHz spectrum of **7** in benzene shows four separate methoxyl signals (see Fig. 4a). For solutions in benzene, the chemical shifts of the methoxyl groups were found to be dependent on the concentration (see Fig. 5), less so than for compounds **5** and **6**, but to a greater extent than for **1** and **2**. Methoxyl signals of **7** showed negligible concentration-dependence in all solvents used, except benzene. Fig. 5 also shows that increase in the ratio of benzene:solute affects the 2- and 3-methoxyl signals of **7** in a similar way, both

being shifted upfield (more than the 4- and 6-methoxyl groups). In addition, the 4-methoxyl signal shows the same concentration-dependence as the 6-methoxyl signal.

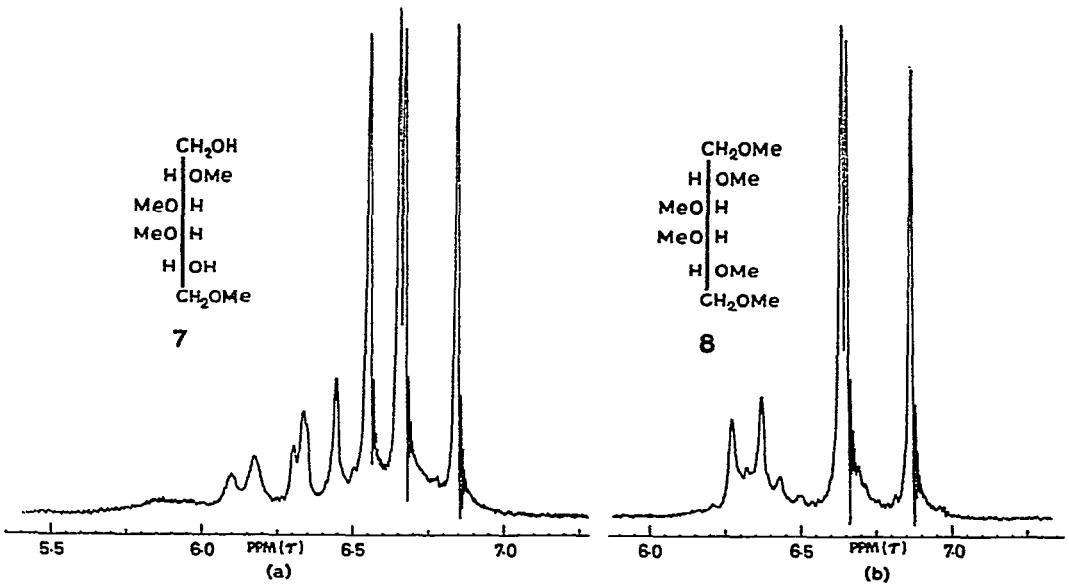

Fig. 4. P.m.r. spectra (60 MHz) of (a) compound 7 and (b) compound 8, in benzene [10% (w/v)] at 26°.

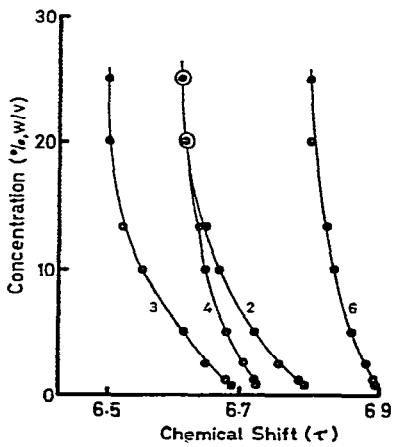

Fig. 5. Concentration-dependence of methoxyl chemical-shifts (numbered 2,3,4, and 6) in the p.m.r. spectrum (60 MHz) of compound 7 in benzene at 26°.

Owing to the simplicity of the methoxyl-signal pattern (a maximum of four signals is observed), use of the p.m.r. spectrum of the derived (deuteriomethyl)ated D-galactitol ether in benzene constitutes a satisfactory method of identifying a methyl ether of D-galactopyranose; it is a method that could conceivably be extended to include other hexose methyl ethers as well.

The p.m.r. spectra of **7** in a number of solvents were recorded (see Table IV). As with **1**, **2**, **5** and **6**, benzene was found to produce the largest spread of the methoxyl-group signals.

TABLE IV

METHOXYL CHEMICAL-SHIFTS[a] FOR COMPOUNDS **7** AND **8**

Solvent	*Compound*	*Chemical shifts of methoxyl groups on carbon atom*					
		1	*2*	*3*	*4*	*5*	*6*
C_6H_6	**7**		6.665	6.55	6.65		6.84
	8	6.85	6.63	6.62	6.62	6.63	6.85
CCl_4	**7**		6.56	6.54	6.56		6.65
	8	6.68	6.63	6.655	6.655	6.63	6.68
$CDCl_3$	**7**		6.50	6.47	6.52		6.60
	8	6.615	6.53	6.555	6.555	6.53	6.615
CH_2Cl_2	**7**		6.55	6.52	6.56		6.635
	8	6.65	6.59	6.62	6.62	6.59	6.65
$(CD_3)_2CO$	**7**		6.58	6.56	6.58		6.67
	8	6.67	6.61	6.63	6.63	6.61	6.67
D_2O	**7**		6.52	6.535	6.545		6.595
	8	6.60	6.55	6.56	6.56	6.55	6.60

[a]Chemical shifts are relative to internal sodium 4,4-dimethyl-4-silapentanesulphonate for solutions in deuterium oxide (τ' scale[1]) and relative to internal tetramethylsilane for the other solutions (τ scale). Shifts in benzene are for 10% solutions at 26°, determined at 60 MHz. Shifts in all other solutions are at 32° and 100 MHz.

*P.m.r. spectra of hexa-*O*-methylgalactitol* (**8**). — The p.m.r. spectrum of **8** (60 MHz, benzene) produces three methoxyl signals only (see Fig. 4b); owing to the symmetry of the molecule, this is found for all solvents used (see Table IV). The p.m.r. spectra of 2,3,4,6-tetra-*O*-methyl-1,5-di-*O*-(methyl-d_3)-D-galactitol (**9**) were used to assign the methoxyl signals in the spectra of **8**. The spectra of **9** show three methoxyl signals, integrating in the ratios of 2:1:1 for all six solvents. The chemical shifts of these signals are the same as those in the corresponding spectra of **8**. For all solvents except benzene, the largest methoxyl signal in the spectrum of **9** (a singlet due to the 3- and 4-methoxyl groups) appears between the 2- and 5-methoxyl signals. The 6-methoxyl group was assigned to the high-field signal, because, although the chemical shift of a methoxyl group is influenced when a neighbouring hydroxyl group is converted into a methoxyl group (as in converting **7** into **8**), the magnitude of the effect in the galactitol methyl ethers investigated[2,4] (in deuterium oxide) is smaller than the difference in chemical shift between the high-field and the other methoxyl signals in the spectrum of **8**. The primary 6-methoxyl group absorbs at highest field in

the p.m.r. spectra of all of the partially methylated galactitols studied[2,4], including that of **7**. From these considerations, the assignment of the methoxyl chemical-shifts of **8** follows automatically.

Variation of methoxyl chemical-shifts with solvent properties. — For solutions in carbon tetrachloride, dichloromethane, and chloroform-*d*, the methoxyl chemical-shifts in the spectra of compounds **1**, **2**, **7**, and **8** decrease as the dipole moment of the C–H or C–D bond in the solvent molecule ($CCl_4 = 0$; $CH_2Cl_2 < CDCl_3$) increases. This trend could be explained by occurrence of stronger hydrogen-bonding between a hydrogen or deuterium atom of the solvent and the oxygen atom of the methoxyl group as this dipole moment increases.

No definite trend was observed when the chemical shifts of the methoxyl groups in compounds **1**, **2**, **7**, and **8** were plotted against such functions[8], of the dielectric constant (ε) of the solvents used, as $(\varepsilon - 1)/(2\varepsilon + 1)$.

EXPERIMENTAL

All 100-MHz p.m.r. spectra were obtained at 32° with a Varian Associates HA-100 instrument. Concentration-dependence studies for benzene solutions were conducted at 60 MHz with a Varian Associates HA-60 instrument at a constant temperature of 26°. A change in temperature was found to affect measurements of chemical shift in benzene and (to a lesser extent) in deuterium oxide, but not in the other solvents used.

The assignment of the methoxyl signals in the p.m.r. spectra of **1** and **2** in benzene was performed as described earlier[5], by use of the following specifically per(deuteriomethyl)ated methyl *O*-methyl-D-galactopyranosides: methyl 2,3,4,6-tetra-*O*-(methyl-d_3)-α-D-galactopyranoside, methyl 2-*O*-methyl-3,4,6-tri-*O*-(methyl-d_3)-α-D-galactopyranoside, methyl 2,3-di-*O*-methyl-4,6-di-*O*-(methyl-d_3)-α-D-galactopyranoside, methyl 2,3,4-tri-*O*-methyl-6-*O*-(methyl-d_3)-α-D-galactopyranoside, methyl 2,3,6-tri-*O*-methyl-4-*O*-(methyl-d_3)-α-D-galactopyranoside, methyl 2-*O*-methyl-3,4,6-tri-*O*-(methyl-d_3)-β-D-galactopyranoside, methyl 2,3-di-*O*-methyl-4,6-di-*O*-(methyl-d_3)-β-D-galactopyranoside, methyl 3,4-di-*O*-methyl-2,6-di-*O*-(methyl-d_3)-β-D-galactopyranoside, and methyl 2,4,6-tri-*O*-methyl-3-*O*-(methyl-d_3)-β-D-galactopyranoside. The procedure was extended to the other solvents specified in Table III. (Deuteriomethyl)ation was effected by an adaptation of the method of Kuhn *et al.*[9].

Acid hydrolysis (5% solutions in 2M hydrochloric acid for 4 h at 100°) of (deuteriomethyl)ated methyl *O*-methyl-D-galactopyranosides yielded the following D-galactopyranose derivatives that were used for assigning the methoxyl signals in the spectra of **5** and **6**: 2-*O*-methyl-3,4,6-tri-*O*-(methyl-d_3)-D-galactopyranose, 2,3-di-*O*-methyl-4,6-di-*O*-(methyl-d_3)-D-galactopyranose, 2,3,4-tri-*O*-methyl-6-*O*-(methyl-d_3)-D-galactopyranose, and 2,3,6-tri-*O*-methyl-4-*O*-(methyl-d_3)-D-galactopyranose.

The following (deuteriomethyl)ated methyl ethers of galactitol were obtained by reduction of the appropriate methyl ethers of D-galactose with sodium borohydride: 2-*O*-methyl-3,4,6-tri-*O*-(methyl-d_3)-D-galactitol; 3,4-di-*O*-methyl-2,6-di-*O*-

(methyl-d_3)-D-galactitol, and 2,4,6-tri-*O*-methyl-3-*O*-(methyl-d_3)-D-galactitol. The p.m.r. spectra of these compounds were used to assign the methoxyl signals in the p.m.r. spectra of **7**.

By (deuteriomethyl)ation of **7**, 2,3,4,6-tetra-*O*-methyl-1,5-di-*O*-(methyl-d_3)-D-galactitol (**9**) was obtained. The p.m.r. spectrum of this compound was used to identify the methoxyl signals in the p.m.r. spectra of **8**, as outlined in the previous section.

Hexa-O-*methylgalactitol* (**8**). — 2,3,4,6-Tetra-*O*-methyl-D-galactitol (**7**) was methylated once with methyl iodide–silver oxide, to produce a syrup that crystallised after three months at room temperature. Compound **8** was obtained as colourless plates, m.p. 45–46°, $[\alpha]_D \pm 0°$ (*c* 0.9, chloroform).

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