P.M.R. SPECTROSCOPY OF TRIMETHYL ETHERS OF D-GALACTOPYRANOSE AND ITS DERIVATIVES

E. B. RATHBONE, A. M. STEPHEN,

C. S. I. R. Carbohydrate Research Unit, Department of Chemistry, University of Cape Town (South Africa)

AND K. G. R. PACHLER

National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria (South Africa)

(Received July 12th, 1971)

ABSTRACT

P.m.r. parameters (determined at 100 MHz for solutions in deuterium oxide) are presented for trimethyl ethers of D-galactopyranose (eight), methyl D-galactopyranoside (eight), and galactitol (four). The anomeric and methoxyl proton chemical-shifts of these compounds are compared with those of the corresponding mono-, di-, and tetra-methyl ethers of D-galactopyranose and its derivatives. The results in this and earlier papers show that anomeric change greatly affects the 2-methoxyl signals (in derivatives of D-galactose, D-glucose, and D-mannose); change in configuration at C-4 (D-galactose compared with D-glucose) affects the neighboring 3-methoxyl signal much more than the 4-methoxyl signal.

INTRODUCTION

In three previous papers, we have described the p.m.r. spectroscopy of monomethyl[1], dimethyl[2], and tetramethyl[3] ethers of D-galactopyranose, methyl α- and β-D-galactopyranoside, and galactitol. P.m.r. spectra of trimethyl ethers of D-galactopyranose and related compounds are now discussed in the light of observations made in the earlier work.

RESULTS AND DISCUSSION

P.m.r. parameters for the following trimethyl ethers of D-galactopyranose and its derivatives are given in Table I: 2,3,4-tri-*O*-methyl-α- and β-D-galactopyranose (**1** and **2**), 2,3,6-tri-*O*-methyl-α- and β-D-galactopyranose (**3** and **4**), 2,4,6-tri-*O*-methyl-α- and β-D-galactopyranose (**5** and **6**) and 3,4,6-tri-*O*-methyl-α- and β-D-galactopyranose (**7** and **8**); methyl 2,3,4-tri-*O*-methyl-α- and β-D-galactopyranoside (**9** and **10**), methyl 2,3,6-tri-*O*-methyl-α- and β-D-galactopyranoside (**11** and **12**), methyl 2,4,6-tri-*O*-methyl-α- and β-D-galactopyranoside (**13** and **14**), and methyl 3,4,6-tri-*O*-methyl-α- and β-D-galactopyranoside (**15** and **16**); and 2,3,4-tri-*O*-methyl-D-galactitol

TABLE I

P.M.R. PARAMETERS[a] FOR TRIMETHYL ETHERS OF D-GALACTOPYRANOSE AND ITS DERIVATIVES

Compound		*Positions of O-methyl substitution*	*H-1*		$J_{1,2}$[b]		*1-OMe*		*2-OMe*		*3-OMe*		*4-OMe*		*6-OMe*	
α	β		α	β	α	β	α	β	α	β	α	β	α	β	α	β
1	**2**	2,3,4	4.575	5.445	3.2	7.5			6.585	6.445	6.53	6.51	6.51	6.50		
3	**4**	2,3,6	4.54	5.40	3.5	7.5			6.57	6.43	6.60	6.58			6.62	6.615
5	**6**	2,4,6	4.57	5.44	3.7	7.8			6.55	6.43			6.51	6.50	6.62	6.615
7	**8**	3,4,6	4.785	5.455	3.6	7.7					6.495[c]	6.48	6.48[c]	6.48	6.60	6.59
9	**10**	1,2,3,4	4.98	5.675	3.0	7.5	6.605	6.460[d]	6.57	6.464[d]	6.53	6.50	6.50	6.495		
11	**12**	1,2,3,6	4.95	5.65	2.5	7.7	6.61	6.44	6.58	6.47	6.60[e]	6.595			6.61[e]	6.605
13[f]	**14**[f]	1,2,4,6	5.00	5.69	3.7	8.0	6.61	6.43	6.56	6.43			6.51	6.49	6.62	6.58
15	**16**	1,3,4,6	5.21	5.71	4.0	7.7	6.58	6.46			6.50	6.50[g]	6.50	6.49[g]	6.60	6.58
17		2,3,4							6.52		6.535		6.535			
18		2,3,6							6.52		6.535				6.60	
19		2,4,6							6.49				6.53		6.59	
20		3,4,6									6.535[h]		6.54[h]		6.59	

[a]Determined at 100 MHz for solutions in deuterium oxide at 32°. Chemical shifts are relative to internal sodium 4,4-dimethyl-4-silapentanesulfonate (τ′ scale). [b]Observed spacings of the doublets (Hz). [c,d,e]These assignments may have to be reversed. [f]Compare with Ref. 4. [g,h]These assignments may have to be reversed.

(**17**), 2,3,6-tri-*O*-methyl-D-galactitol (**18**), 2,4,6-tri-*O*-methyl-D-galactitol (**19**), and 3,4,6-tri-*O*-methyl-D-galactitol (**20**).

The effects of introducing additional methoxyl groups into the derivatives of D-galactopyranose described earlier[1,2] were investigated by comparing the results found for the mono- and di-methyl ethers with those in Table I.

P.m.r. spectra of trimethyl ethers of D-*galactopyranose.* — (*a*) *Assignment of methoxyl signals.* 2,3,4-Tri-*O*-methyl- and 2,4,6-tri-*O*-methyl-D-galactopyranose both crystallized as the α anomer (**1** and **5**, respectively), permitting the equilibration of their solutions in deuterium oxide to be monitored, and the methoxyl signals of the β anomers to be distinguished from those of the α anomers. 2,3,6-Tri-*O*-methyl- and 3,4,6-tri-*O*-methyl-D-galactopyranose were obtained as equilibrated syrups. Signals due to the two anomeric forms could, however, be distinguished by noting that, for both these compounds, there is a greater proportion of the β than of the α anomer at equilibrium.

All methoxyl signals in the spectra of **1** and (**1**+**2**) were identified by comparing them with those of the 2-, 3-, and 4-methoxyl groups in the spectrum of 2,3,4,6-tetra-*O*-methyl-D-galactopyranose[3] and by assuming that methylation at O-6 has no effect on the 2-, 3-, and 4-methoxyl signals.

The four low-field, methoxyl signals in the spectrum of 2,3,6-tri-*O*-methyl-D-galactose have the same chemical shifts as the methoxyl groups of 2,3-di-*O*-methyl-D-galactose[2]. Hence, these signals were attributed to the 2- and 3-methoxyl groups of **3** and **4**, and the remaining two upfield signals to the 6-methoxyl groups.

Methoxyl signals for **5** and **6** were obtained by comparing the spectra of **5** and (**5**+**6**) with those of 2,4- and 4,6-di-*O*-methyl-D-galactopyranose[2]. The chemical shifts of the methoxyl groups of 2,4,6-tri-*O*-methyl-D-galactopyranose (no neighboring methoxyl groups) are very similar to those of the monomethyl ethers[1] 2-*O*-methyl-D-galactose, 4-*O*-methyl-D-galactose, and 6-*O*-methyl-D-galactose, respectively.

The p.m.r. spectrum of 3,4,6-tri-*O*-methyl-D-galactopyranose (**7**+**8**) showed only four distinguishable signals attributable to methoxyl groups, the two upfield signals being due to the (primary) 6-methoxyl groups (by comparison with the spectrum of 2,3,4,6-tetra-*O*-methyl-D-galactose[3]). Of the other two, one was equivalent to three methoxyl groups, and the other, about 0.01 p.p.m. upfield, to one methoxyl group. By making a comparison with the spectrum of 2,3,4,6-tetra-*O*-methyl-D-galactose, the 3-methoxyl group of **7** was attributed to the upfield signal, and the other to the 3- and 4-methoxyl groups of **8** and the 4-methoxyl group of **7**.

(*b*) *Chemical shifts of anomeric protons.* The effects on the chemical shifts of H-1 for mono-[1] and di-methyl[2] ethers of D-galactopyranose apply to the trimethyl ethers as well; for compounds having a methoxyl group on C-2 (**1**–**6**), the anomeric protons appear at τ' 4.54–4.57 (α anomers) and τ' 5.40–5.44 (β anomers), a difference of 0.87 p.p.m. on the average; when there is a hydroxyl group on C-2 (**7** and **8**), the H-1 chemical-shift is at higher field by 0.22–0.25 p.p.m. (α anomers) and 0.01 to 0.06 p.p.m. (β anomers).

The observed spacings of the anomeric proton doublets ($J_{1,2}$) indicate that

the *C1* (D) conformation of the D-galactopyranose is retained, with possibly only minor distortions, as hydroxyl groups are successively methylated.

(*c*) *Chemical shifts of methoxyl-group protons.* The observations made earlier[1–3] concerning the influence of methylation of an adjacent hydroxyl group, or of change in configuration of adjacent hydroxyl or methoxyl groups, on the chemical shift of a methoxyl group are confirmed for the trimethyl ethers of D-galactopyranose. The presence of a third methoxyl group does not alter the effects noted for the dimethyl ethers of D-galactopyranose. The only significant effects in the trimethyl ethers are (*a*) change in configuration at C-1 from α to β produces a downfield shift of the equatorial 2-methoxyl signal of 0.12 p.p.m., and (*b*) methylation at O-4 (axial) produces a downfield shift of 0.09–0.10 p.p.m. in the signal of the equatorial 3-methoxyl group. Anomeric change does not significantly affect the 3-, 4-, and 6-methoxyl signals, the signals due to the β anomers usually appearing at only slightly lower field (0–0.02 p.p.m.). The (primary) 6-methoxyl signals appear at highest field (τ′ 6.59–6.62 for **3**–**8**).

Comparison of the spectra of compounds **1**–**8** with those of 2,3,4,6-tetra-*O*-methyl-α- and β-D-galactopyranose[3] shows that only the 3-methoxyl signals of compounds **3** and **4** are significantly affected (shifted downfield ~0.07 p.p.m. by methylation at O-4) by the formation of the tetramethyl ether of α- or β-D-galactopyranose.

P.m.r. spectra of trimethyl ethers of methyl D-*galactopyranoside.* — (*a*) *Assignment of methoxyl signals.* The p.m.r. spectra of compounds **9**–**14** and **16** were obtained for the pure methyl α- and β-glycosides. P.m.r. parameters for **15** were deduced from the spectrum of a mixture of the α- and β-glycosides (see Experimental section). The methoxyl signals of **9** and **10** were identified by comparison with the 1-, 2-, 3-, and 4-methoxyl signals in the spectra of methyl 2,3,4,6-tetra-*O*-methyl-α- and β-D-galactopyranoside[3]. The methoxyl-group assignments for methyl 2,3-di-*O*-methyl-α- and β-D-galactopyranoside[2] were used for obtaining the methoxyl signals for **11** and **12** (on the assumption that methylation at O-6 does not affect the chemical shifts of the 1-, 2-, and 3-methoxyl groups). The spectra of methyl 2,4-di-*O*-methyl-α- and β-D-galactopyranoside[2] and methyl 4,6-di-*O*-methyl-α- and β-D-galactopyranoside[2] permitted methoxyl signals to be assigned in the spectra of **13** and **14**. The spectra of **15** and **16** were compared with those of methyl 3,4-di-*O*-methyl-α- and β-D-galactopyranoside[2] (to identify the 1-, 3-, and 4-methoxyl signals), methyl 4,6-di-*O*-methyl-α- and β-D-galactopyranoside[2] (to identify the 6-methoxyl signals), and methyl 2,3,4,6-tetra-*O*-methyl-α- and β-D-galactopyranoside[3] (to confirm the assignments made for the 4- and 6-methoxyl groups).

(*b*) *Chemical shifts of anomeric protons.* The observations just made in section (*b*), regarding the influence of methylation at O-2 on the chemical shifts of the anomeric protons in the spectra of the D-galactopyranose methyl ethers, apply equally to their methyl glycosides. The formation of the methyl glycosides produces an upfield shift of 0.41–0.43 p.p.m. (α glycosides) and 0.23–0.26 p.p.m. (β glycosides) in

the H-1 signals. As before, there are small differences in the spacings of the H-1 doublets ($J_{1,2}$).

(*c*) *Chemical shifts of methoxyl-group protons.* The introduction of a methoxyl group at C-1 has very little influence on the 2-, 3-, 4-, and 6-methoxyl signals in the spectra of compounds **1–8**.

The effects of change in configuration at C-1, and of methylation of adjacent hydroxyl groups, on the chemical shift of a methoxyl group agree with those noted in the previous subsection (*c*), and for the mono-[1], di-[2], and tetra-methyl[3] ethers of methyl D-galactopyranoside.

Methylation of the hydroxyl group in compounds **9–16** to afford either methyl 2,3,4,6-tetra-*O*-methyl-α- or β-D-galactopyranoside[3] has a significant effect on the chemical shift of the 3-methoxyl groups of **11** and **12** only, these signals being shifted downfield by 0.06–0.08 p.p.m. A similar observation was made earlier[2], and in subsection (*c*) of the preceding section.

P.m.r. spectra of trimethyl ethers of galactitol. — (*a*) *Assignment of methoxyl signals.* The spectrum of **17** showed two signals for the three methoxyl groups. The low-field signal (3 H) was attributed to the 2-methoxyl group (by comparison of the spectrum with that of 2,3,4,6-tetra-*O*-methyl-D-galactitol[3]). Signals for the 2- and 3-methoxyl groups in the spectrum of **18** were obtained by comparison with the spectrum of 2,3-di-*O*-methyl-D-galactitol[2], on the assumption that methylation at O-6 does not affect the chemical shifts of the 2- and 3-methoxyl groups. The spectra of 2,4- and 4,6-di-*O*-methyl-D-galactitol[2] were used for identifying the methoxyl signals in the spectrum of **19**. The 4- and 6-methoxyl signals of **20** were obtained by comparison with the spectrum of 2,3,4,6-tetra-*O*-methyl-D-galactitol[3]. There is some uncertainty as to the assignments for the 3- and 4-methoxyl groups of **20**, the signals being separated by less than 0.01 p.p.m.

(*b*) *Chemical shifts of methoxyl-group protons.* Comparison of the methoxyl chemical-shifts of galactitol methyl ethers given in earlier papers[1–3] with those of the trimethyl ethers shows that the (primary) 6-methoxyl and 1-methoxyl groups absorb in the region τ' 6.59–6.61, that is, 0.04–0.10 p.p.m. upfield from the secondary 2-, 3-, 4-, and 5-methoxyl groups (τ' 6.49–6.56). The 2- and 5-methoxyl signals appear at slightly lower field than those of the other secondary methoxyl groups. The introduction of *O*-methyl groups into a partially methylated galactitol derivative has negligible effect on the chemical shifts of adjacent methoxyl groups. There does, however, appear to be a general increase in the chemical shifts of the secondary (2-, 3-, and 4-) methoxyl groups as the number of methoxyl groups is increased.

Methoxyl-group chemical-shifts of intermediates used in the synthesis of methyl ethers of D-*galactose and its derivatives.* — From Table II, and related tables in earlier papers[1,2], it may be seen that the spread of methoxyl signals for many of the intermediates (in chloroform-*d*) is significantly greater than that of corresponding methyl ethers (in deuterium oxide) lacking aromatic substituents. This observation suggests an extension (of the present approach to the identification of methyl ethers of sugars)

TABLE II

P.M.R. PARAMETERS[a] FOR INTERMEDIATES USED IN THE SYNTHESIS OF TRIMETHYL ETHERS OF D-GALACTOPYRANOSE AND ITS DERIVATIVES

Compound	*Solvent*	*Galactose C–H protons*	J	*Methoxyl protons*[b]	*Substituent protons*[c]
21	$CDCl_3$	H-1, 5.25; other, 5.8–6.8	$J_{1,2}$ 2.2	C-1, 6.63	trityl, 2.3–2.9(m)
22	$CDCl_3$	H-1, 5.89; other, 6.1–6.9	$J_{1,2}$ 7.0	C-1, 6.50	trityl, 2.4–2.9(m)
23	$CDCl_3$	H-1, 5.02; other, 5.6–6.6	$J_{1,2}$ 3.5	C-2, 6.49 C-1, 6.56	C_6H_5CH, 2.3–2.7(m); C_6H_5CH, 4.44; (OH, 7.22)
24	$CDCl_3$	H-1, 5.11; other, 5.0–6.5	$J_{1,2}$ 3.3	6.63, 6.75	tosyl[d] (aromatic), 2.22 (d, 2 H), 2.76 (d, 2 H), *J* 8.0; tosyl Me, 7.63; C_6H_5CH, 2.6–2.8(m); C_6H_5CH, 4.62
25	$CDCl_3$	H-1, 5.08; other, 5.0–6.6	$J_{1,2}$ 3.2	6.61, 6.81	tosyl (aromatic), 2.12 (d, 2 H), 2.64 (d, 2 H), *J* 8.2; tosyl Me, 7.56; [OH, 6.96 (2 H)]
26	$CDCl_3$	H-1, 5.17; H-2, 6.23; H-3, 5.175; other, 6.0–6.9	$J_{1,2}$ 3.9, $J_{2,3}$ 10; $J_{3,4}$ 3.2	6.38, 6.61, 6.64, 6.81	tosyl (aromatic), 2.16 (d, 2 H), 2.70 (d, 2 H), *J* 8.4; tosyl Me, 7.56
27	$CDCl_3$	H-1, 5.785; H-2, 6.715; other, 5.5–6.9	$J_{1,2}$ 7.4, $J_{2,3}$ 9.5	6.38, 6.44	C_6H_5CH, 2.3–2.7; C_6H_5CH, 4.45; (OH, 7.34).
28	$CDCl_3$	H-1, 5.83; H-2, 6.59; H-3, 5.47; other, 5.6–6.8	$J_{1,2}$ 7.7; $J_{2,3}$ 9.6; $J_{3,4}$ 3.6	6.52, 6.73	C_6H_5CH, 2.4–2.9; C_6H_5CH, 4.64; tosyl (aromatic), 2.18 (d, 2 H), 2.75 (d, 2 H), *J* 8.2; tosyl Me, 7.64
29	$CDCl_3$	H-1, 5.81; H-2, 6.68; H-3, 5.59; other, 5.7–6.9	$J_{1,2}$ 8.2; $J_{2,3}$ 9.5; $J_{3,4}$ 3.4	6.49, 6.84	tosyl (aromatic), 2.18 (d, 2 H), 2.67 (d, 2 H), *J* 8.3; tosyl Me, 7.57; (OH, 6.89)
30	$CDCl_3$	H-1, 5.87; H-2, 6.71; H-3, 5.59; H-4, 6.195; other, 6.2–6.8	$J_{1,2}$ 7.5; $J_{2,3}$ 9.8; $J_{3,4}$ 3.2 $J_{4,5}$ ~1	6.39, 6.515, 6.60, 6.80	tosyl (aromatic), 2.15 (d, 2 H), 2.65 (d, 2 H), *J* 8.4; tosyl Me, 7.545
31	$CDCl_3$	5.3–6.8		C-1, 6.70	tosyl (aromatic), 2.15 (d, 2 H), 2.66 (d, 2 H), *J* 8.3; tosyl Me, 7.58; CMe_2, 8.50, 8.68; trityl, 2.4–2.9 (m)
32	D_2O	5.1–6.5		C-1, 6.84	tosyl (aromatic), 2.15 (d, 2 H), 2.54 (d, 2 H), *J* 8.3; tosyl Me, 7.58
33	$CDCl_3$	H-1, 5.81; H-2, 5.25; other, 6.2–6.9	$J_{1,2}$ 7.8; $J_{2,3}$ 9.6	6.44, 6.61, 6.655 6.79	tosyl (aromatic), 2.18 (d, 2 H), 2.72 (d, 2 H), *J* 8.3; tosyl Me, 7.565

[a]Determined at 60 MHz and 37°. Chemical shifts are relative to internal tetramethylsilane (τ scale) for solutions in chloroform-*d*, and relative to sodium 4,4-dimethyl-4-silapentanesulfonate (τ' scale) for the solution in deuterium oxide, *J* = observed spacing (Hz). [b]3-Proton singlets. [c]Singlets, unless otherwise stated; d = doublet, m = multiplet. [d]*p*-Tolylsulfonyl.

to examination of the p.m.r. spectra of suitably selected derivatives having substituents so chosen as to give as wide a spread of the methoxyl-group chemical-shift as is practicable.

EXPERIMENTAL

Compounds **9**, **10**, **13**, **14**, and **16** were synthesized by known methods, with modifications as indicated. P.m.r. parameters for the intermediate compounds **21**–**33** used in the synthesis of these trimethyl ethers of methyl α- and β-D-galactopyranoside are collected in Table II.

Methyl 2,3,4-tri-O-*methyl*-α-D-*galactopyranoside* (**9**). — Methylation of methyl 6-*O*-trityl-α-D-galactopyranoside[5] (**21**) afforded methyl 2,3,4-tri-*O*-methyl-6-*O*-trityl-α-D-galactopyranoside; this was hydrolyzed with 90% trifluoroacetic acid[6] to give[5] **9**.

Methyl 2,3,4-tri-O-*methyl*-α-D-*galactopyranoside* (**10**). — Compound **10** (Ref. 7) was prepared as for **9**, starting with methyl 6-*O*-trityl-β-D-galactopyranoside[8] (**22**).

Methyl 2,3,6-tri-O-*methyl*-α-D-*galactopyranoside* (**11**). — Partial methylation of methyl α-D-galactopyranoside with dimethyl sulfate–sodium hydroxide for 50 h produced a mixture of methyl ethers of the starting material [t.l.c.; silica gel, 5:1 (v/v) chloroform–methanol]. The neutralized mixture was extracted with chloroform, the extract was evaporated under diminished pressure, the residual syrup was dissolved in water, and the solution was continuously extracted with petroleum ether (b.p. 60–80°) for 10 h. The extract was evaporated to a syrup which was dissolved in water; the solution was extracted with chloroform, and the extract was evaporated to a syrup that was shown by g.l.c. to consist mainly[9] of **11**.

Methyl 2,3,6-tri-O-*methyl*-β-D-*galactopyranoside* (**12**). — By use of methyl β-D-galactopyranoside as the starting material, compound **12** (Ref. 9) was synthesized as for compound **11**.

Methyl 2,4,6-tri-O-*methyl*-α-D-*galactopyranoside* (**13**). — Methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-galactopyranoside[10] (**23**) was *p*-toluenesulfonylated, yielding methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside[10] (**24**). Hydrolysis of **24** with 90% trifluoroacetic acid[6] afforded methyl 2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside (**25**), which was methylated to give methyl 2,4,6-tri-*O*-methyl-3-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside[10] (**26**). Desulfonylation of **26** with sodium methoxide produced **13** (Ref. 10).

Methyl 2,4,6-tri-O-*methyl*-β-D-*galactopyranoside* (**14**). — *p*-Toluenesulfonylation of methyl 4,6-*O*-benzylidene-2-*O*-methyl-β-D-galactopyranoside[10] (**27**) gave methyl 4,6-*O*-benzylidene-2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside[10] (**28**), which was hydrolyzed with 90% trifluoroacetic acid[6] to produce methyl 2-*O*-methyl-3-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside (**29**). Methylation of **29** yielded methyl 2,4,6-tri-*O*-methyl-3-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside[10] (**30**), which was reductively desulfonylated with sodium methoxide in methanol to give **14** (Ref. 10).

Methyl 3,4,6-tri-O-*methyl*-β-D-*galactopyranoside* (**16**). — Methyl 3,4-*O*-iso-

propylidene-6-*O*-trityl-β-D-galactopyranoside[1] was *p*-toluenesulfonylated to give methyl 3,4-*O*-isopropylidene-2-*O*-*p*-tolylsulfonyl-6-*O*-trityl-β-D-galactopyranoside[11] (**31**). Hydrolysis of **31** with 90% trifluoroacetic acid[6] afforded methyl 2-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside[11] (**32**); this was methylated, yielding methyl 3,4,6-tri-*O*-methyl-2-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside[12] (**33**). Reductive desulfonylation whith sodium methoxide in methanol gave pure **16**, as indicated by g.l.c.

A mixture (~4:1) of **15** and **16** was produced by treatment of **16** with methanolic hydrogen chloride (2%). The p.m.r. spectrum of this mixture was used for obtaining the p.m.r. parameters for **15**.

General. — Hydrolysis of **13** and **16** with 0.5M sulfuric acid produced 2,4,6-tri-*O*-methyl-D-galactopyranose[10] (**5**+**6**) and 3,4,6-tri-*O*-methyl-D-galactopyranose[13] (**7**+**8**), respectively.

Galactitol methyl ethers were prepared by reduction[14] of the appropriate trimethyl ethers of D-galactopyranose with sodium borohydride.

100-MHz spectra (see Table I) were recorded with a Varian Associates HA-100 n.m.r. spectrometer for 5–10% solutions in deuterium oxide at 32°. Sodium 4,4-dimethyl-4-silapentanesulfonate was used as the internal standard (τ' scale). 60-MHz spectra of the intermediates (see Table II) were recorded at 37° with a Varian Associates A-60 n.m.r. spectrometer.

Gas–liquid chromatography (g.l.c.) was performed with a Beckman GC-2A instrument, the column containing 14% of poly(ethylene glycol succinate) on acid-washed Chromosorb W at 160°.

ACKNOWLEDGMENTS

We are indebted to Miss M. J. Cooper and Dr. P. L. Wessels (National Chemical Research Laboratory, C.S.I.R.) for recording the 100-MHz p.m.r. spectra.

Financial assistance was received from the C.S.I.R. and the University of Cape Town (Staff Research Fund).

REFERENCES

1 E. B. RATHBONE, A. M. STEPHEN, AND K. G. R. PACHLER, *Carbohyd. Res.*, 20 (1971) 357.
2 E. B. RATHBONE, A. M. STEPHEN, AND K. G. R. PACHLER, *Carbohyd. Res.*, 21 (1972) 73.
3 E. B. RATHBONE, A. M. STEPHEN, AND K. G. R. PACHLER, *Carbohyd. Res.*, 20 (1971) 141.
4 S. A. BARKER, J. HOMER, M. C. KEITH, AND L. F. THOMAS, *J. Chem. Soc.*, (1963) 1538.
5 F. SMITH, *J. Chem. Soc.*, (1939) 1724.
6 J. E. CHRISTENSEN AND L. GOODWIN, *Carbohyd. Res.*, 7 (1968) 510.
7 M. ONUKI, *Bull. Inst. Phys. Chem. Res.* (Tokyo), 12 (1933) 614.
8 A. MÜLLER, *Ber.*, 64 (1931) 1820.
9 N. R. WILLIAMS AND R. W. JEANLOZ, *J. Org. Chem.*, 29 (1964) 3434.
10 D. J. BELL AND S. WILLIAMSON, *J. Chem. Soc.*, (1938) 1196.
11 J. S. D. BACON, D. J. BELL, AND H. W. KOSTERLITZ, *J. Chem. Soc.*, (1939) 1248.
12 L. F. WIGGINS, *J. Chem. Soc.*, (1944) 522.
13 R. KUHN AND H. H. BAER, *Chem. Ber.*, 88 (1955) 1537.
14 M. L. WOLFROM AND A. THOMPSON, *Methods Carbohyd. Chem.*, 2 (1963) 67.