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Note

Synthesis and carbon-13 n.m.r.-spectral study of methyl 2,6- and 3,6-dideoxy-α-L-*arabino*- and methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside

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Dideoxy sugars frequently occur as components of several important natural compounds, such as antibiotics, plant glycosides, and bacterial cell-wall polysaccharides[1,2]. In contrast to their importance, the synthesis of only a few of them has been achieved, mainly by rather individual routes. This is partly due to the fact that no generally applicable, rational procedure has been available for deoxygenation of carbohydrates at a secondary position, and partly to the lack, in the case of several monosaccharides, of partially protected derivatives suitable for deoxygenation at the desired positions. On the other hand, although a large amount of ^{13}C-n.m.r.-spectral data has been accumulated in the carbohydrate field[3], only a very few ^{13}C-n.m.r. data are available for dideoxy sugars.

In the present Note, we describe the synthesis of the title glycosides, starting from partially protected L-rhamnose derivatives, namely, methyl 2,4-di-*O*-benzyl-^{4a,5,6} (**1**), methyl 3,4-di-*O*-benzyl-^{4a,5,6} (**2**), and methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[7] (**6**), and using the radical-mechanism, deoxygenation procedure of Barton and McCombie[8], and we discuss the analysis of their ^{13}C-n.m.r. spectra.

EXPERIMENTAL

General. — Except for compounds **11**, **12**, and **14**, all compounds described herein were syrups. The syrupy compounds were dried at ~30° and at 15–20 Pa. Optical rotations were measured with a Perkin–Elmer 241 automatic polarimeter for solutions in chloroform (unless otherwise stated) in concentrations between 0.5 and 2.0. Thin-layer chromatography was performed on precoated layers of silica gel (Merck), with detection by charring with 50% aqueous sulfuric acid or by quenching of ultraviolet light in the case of the benzylated derivatives. Kieselgel H was

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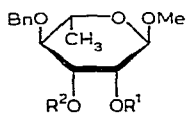
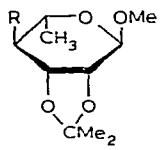
used for column chromatography. ^{1}H-N.m.r. spectra were recorded, for solutions in chloroform-*d* (internal tetramethylsilane) at room temperature, with a Jeol MH-100 instrument at 100 MHz. ^{13}C-N.m.r. spectra were recorded with a Varian XL-100-FT spectrometer at 25.16 MHz, for solutions in chloroform-*d* in spinning tubes (5 mm) at 50°, using 8k data points, with proton–noise decoupling. Coupling constants ($^1J_{C,H}$) were determined by the gated-decoupling technique. Chemical shifts in p.p.m. are given relative to internal tetramethylsilane.

Compounds. — Compound **1*** was obtained[4a] in 70% yield from the readily available methyl 4-*O*-benzyl-α-L-rhamnopyranoside[9] (**3**) by phase-transfer-catalyzed benzylation with benzyl bromide; in this reaction, compound **2** was also formed*.

We obtained **2** in a 50% (overall) yield from **3** by the phase-transfer-catalyzed

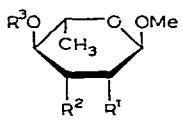


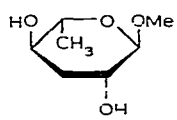


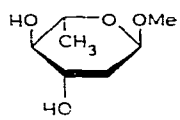
	R^1	R^2
1	Bn	H
2	H	Bn
3	H	H
4	Bn	CSSMe
5	CSSMe	Bn

Bn = $PhCH_2$

6 R = OH
7 R = OCSSMe
8 R = H



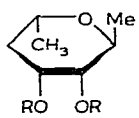


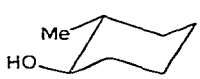


	R^1	R^2	R^3
9	OBn	H	Bn
10	H	OBn	Bn
11	OH	OH	H

12

13





14 R = H
15 R = Bn

16

17

*A recent publication[6] described the synthesis of **1** in a way practically identical with our previous description[4a], confirming our published observation of the isomeric distribution of **1** and **2** in this reaction. Also, the synthesis of **2** *via* the dibutylstannylene derivative of **3** was reported[6], under experimental conditions somewhat different from those we used.

TABLE I

^{1}H-N.M.R. DATA ON THE COMPOUNDS REPORTED HEREIN

Compound	^{1}H-n.m.r. data[a]												[α]$_D$ (degrees)	Chromatographic solvent[b]	Yield (%)	References
	H-1	*H-2a*	*H-2e*	*H-3a*	*H-3e*	*H-4e*	*H-4a*	*H-5*	*H-6*	*O-CH$_3$*	*S-CH$_3$*	*(H$_3$C)$_2$C*				
1													−15	A	70	4a,5,6
2													−44	A	65	4a,5,6
4			4.04–4.14	6.01 $J_{2,3}$ 3.3 $J_{3,4}$ 9.5			3.65 ⟷	3.85 ⟷	1.34	3.30	2.52		−4.4	A	91	
5			6.12	4.00 $J_{2,3} \sim 4$ $J_{3,4} \sim 10$			3.46	3.76	1.32	3.32	2.52		−4.4	A	95	
7	4.50		4.1 ⟷	4.4 ⟷			5.86 $J_{3,4} \sim 7$	3.85 $J_{4,5} \sim 10$	1.22	3.40	2.58	1.38 1.58	−42	A	90	
9			3.35–3.8	1.70 $J_{2,3a}$ 3 $J_{3a,3e}$ 13.7 $J_{3a,4}$ 10.4	2.23 $J_{2,3e}$ – $J_{3e,4} \sim 4$		3.35 ⟷	3.8 ⟷	1.32	3.34			-58	B	51	
10		1.66 $J_{2a,2e}$ 12.7 $J_{2a,3}$ 11 $J_{1,2a}$ 3.7	2.27 $J_{2e,3}$ 5.2 $J_{1,2e}$ 1.3	3.5–4.1			3.1 $J_{3,4} = J_{1,5} = \sim 10$	3.5–4.1	1.28	3.18			−73	A	45	
8	4.9		3.6 ⟷	4.4 ⟷		1.5 ⟷	2.0 ⟷	3.6–4.4	1.22	3.36		1.32 1.50	−65	A	70	
12[c]	4.46		3.2–3.9	1.6 ⟷	2.1 ⟷		3.2 ⟷	3.9 ⟷	1.27	3.36			−80.5 −102 (H$_2$O)	C	72	18a
13[d]														C	75	17b
14[e]	4.75		3.5 ⟷	4.1 ⟷		1.4 ⟷	1.8 ⟷	3.5–4.1	1.24	3.35			-83 -72 (H$_2$O)	C	60	

[a]Chemical shifts in p.p.m., relative to internal tetramethylsilane; coupling constants in Hz. [b]*A*, 3:2 light petroleum–ethyl acetate; *B*, 4:1 light petroleum–ethyl acetate; *C*, 4:1 benzene–methanol. [c]M.p. 82°. [d]For physical data, see ref. 17b. [e]M.p. 99–100.5°.

allylation (with allyl bromide, at HO-2; see ref. 4a), benzylation (benzyl chloride–KOH), and deallylation (with Pd–C, in aqueous ethanol containing acetic acid) sequence[4b]. Compound **2** was also prepared by benzylation, with benzyl bromide, of the dibutylstannylene derivative of **3** at 90°, without any additional solvent. By this modification*, we obtained **2** in 65% yield from **3**.

Conversion of **1**, **2**, and **6** into the corresponding *O*-(methylthio)thiocarbonyl derivatives (**4**, **5**, and **7**, respectively) was achieved in 90–95% yields (see Table I). Treatment of **4**, **5**, and **7** with tributyltin hydride, according to the published procedure[8], gave the desired dideoxy derivatives (**9**, **10**, and **8**) in 46–70% yields. In this reaction, a small proportion of the parent alcohols (**1**, **2**, and **6**) was also formed (10–20%).

This side reaction was found to occur in a related reaction reported by Horton and co-workers[12], but was apparently absent when 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-(*S*-methyl dithiocarbonate) was treated[8] with tributyltin hydride, or when several hexofuranosyl (*gluco*-, *allo*-, and *galacto*-) 3-(*S*-methyl dithiocarbonates) were reduced with tributyltin deuteride[13]. The benzyl protecting-groups were stable under the conditions of the reduction. Catalytic hydrogenolysis of the benzyl-protected derivatives (**9** and **10**) in ethanol, under atmospheric pressure and at room temperature in the presence of 10% Pd–C, gave the 3,6- (**12**) and 2,6-dideoxyglycoside (**13**), respectively, and treatment of **8** with trifluoroacetic acid yielded the 4,6-dideoxy derivative (**14**). Physical data, yields, and solvents used for the column-chromatographic purification of the compounds described in this paper are given in Table I.

Neither polar nor steric effects seem to affect this deoxygenation reaction, and the route proposed here may be successfully applied to removal of the hydroxyl group from any secondary carbon atom of the rhamnopyranose ring**. In addition to the isopropylidene group[8,12,13], the benzyl group may be used to protect the other secondary hydroxyl groups under the conditions of the reduction.

RESULTS AND DISCUSSION

The ^{13}C-n.m.r.-spectral data for the dideoxy sugars, together with those for

*Alkylations of the dibutylstannylene derivatives are usually conducted in such solvents as 1,4-dioxane or *N*,*N*-dimethylformamide[10]. In addition to this reaction, we have also found[11] that the dibutylstannylene derivative of **3** can be methylated with methyl iodide without additional solvent, to give the 3-*O*-methyl derivative in excellent yield.

**In contrast to the foregoing radical-mechanism reduction-process, SN2-type reactions are rather difficult to carry out for L-rhamnopyranoses. It is well known that such processes are generally hindered, mainly by polar effects, at C-2 of an aldohexopyranose. In fact, we observed no substitution reaction when methyl 4-*O*-benzyl-3-*O*-methyl-2-*O*-*p*-tolylsulfonyl-α-L-rhamnopyranoside (obtained from methyl 4-*O*-benzyl-2-*O*-*p*-tolylsulfonyl-α-L-rhamnopyranoside[14a]) was treated with various nucleophilic agents under a variety of conditions. Moreover, attempted substitution of the trifluoromethylsulfonyloxy group at C-3 of an L-rhamnopyranoside derivative with hydride anion yielded[14] an L-*lyxo*-pentofuranoside derivative, presumably by participation of the electrons of the C-4–C-5 bond, and attempted substitution of a sulfonyloxy group at C-4 in L-rhamnopyranose derivatives led[15] to rearranged products, by oxygen-atom participation.

TABLE II

^{13}C-N.M.R. DATA[a] FOR THE COMPOUNDS REPORTED HEREIN

Atom	*Compound*										
	11[16]	**14**	**12**	**13**	**1**[5]	**9**	**2**[5]	**10**	**8**	**A**[b]	**15**
C-1	101.1[c]	101.9	100.3	98.6[d]	98.3	98.4[e]	100.5	98.4	99.1	99.3	100.5
C-2	71.0	68.8	68.4*	37.9	78.9	75.4*	68.6	35.9	73.0	74.6	74.5
C-3	71.8	66.0	35.2	69.2	71.7	29.7	80.2	77.5	71.2	80.0	70.3
C-4	73.0	36.2	69.7*	78.1	82.2	75.6*	80.2	84.4	36.3	71.9	34.3
C-5	68.2	64.3	67.7	67.7	67.3	68.2	67.4	67.2	62.1	68.6	64.9
C-6	17.54	21.11	17.79	17.79	18.09	18.18	17.99	18.27	21.31	17.83	21.27
O-CH_3	54.8	54.7	54.7	54.6	54.6	54.4	54.6	54.4	54.7	54.6	54.5
CH_2-2					73.1	71.2			108.8[f]	72.7	
CH_2-3							72.0	71.8	28.2[f]	71.7	
CH_2-4					74.8	71.2	75.2	75.1	26.3[f]		

[a]The assignments marked with an asterisk may be reversed in each vertical column. [b]A, methyl 2,3-di-*O*-benzyl-α-L-rhamnopyranoside. [c]$^1J_{C-1,H-1}$ 167.5 Hz. [d]$^1J_{C-1,H-1}$ 168.5 Hz. [e]$^1J_{C-1,H-1}$ 166.2 Hz. [f]Isopropylidene carbon atoms.

TABLE III

DIFFERENCE BETWEEN THE ^{13}C-N.M.R. CHEMICAL SHIFTS FOR METHYL α-L-RHAMNOPYRANOSIDE AND **12**, **13**, AND **14** (IN p.p.m.)[a]

Compound	*Atom*					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
12	−0.2	− 2.6	+36.6	+ 3.3	+0.5	−0.3
13	+2.5	+33.1	+ 2.6	− 5.1	+0.5	−0.3
14	−0.8	− 2.2	+ 5.8	−36.8	+3.9	−3.6

[a]The positive sign indicates an upfield shift for the dideoxy derivatives, relative to methyl α-L-rhamnopyranoside.

some reference compounds, are given in Table II, and Table III shows the difference between the ^{13}C-n.m.r. chemical-shifts of the dideoxyglycosides **12**, **13**, and **14** and methyl α-L-rhamnopyranoside (**11**). In the ^{13}C-n.m.r. spectra of methyl 2,6- (**13**) and 3,6-dideoxy-α-L-*arabino*-hexopyranoside (**12**) and methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside (**14**), the assignments of the lines to the C-6 (methyl), CH_2, and anomeric carbon atoms are straightforward, due to their characteristic, chemical-shift ranges (see ref. 1 in ref. 3).

In the spectra of **12** and **13**, the lines at 67.7 p.p.m. are assigned to C-5, which is only slightly affected by the removal of the hydroxyl group from relatively remote carbon atoms (C-3 and C-2, respectively); this resonance lies only 0.5 p.p.m. to

higher field than the corresponding one for **11**. For **14**, the signal at 64.3 p.p.m. is assigned to C-5, and that at 66.0 p.p.m., to C-3. These assignments are made on the basis of the chemical-shift data for **11**, in which C-5 is more shielded than C-3. For **13**, the line at 78.1 p.p.m. is attributed to C-4, an atom that, in **11**, gives rise to a resonance at 73.0 p.p.m. The downfield shift of 5.1 p.p.m. observed is considered to be a consequence of the loss of 1,3-*cis*-diaxial interaction between HO-2 and H-4, through which the effect of HO-2 is experienced by C-4. For **13**, the line at 69.2 p.p.m. is assigned to C-3, the upfield shift of 2.6 p.p.m. of this carbon atom relative to that in **11** being attributed to the loss of the effect of HO-2.

For **12**, both C-2 and C-4 are more shielded than the corresponding atoms in **11**, again because of the loss of the effect of the hydroxyl group. These lines could not, however, be assigned unequivocally to the individual carbon atoms. The data in Table III show that removal of the hydroxyl group causes, in addition to a large (33–37 p.p.m.) upfield-shift of the *alpha*-carbon atom, a significant upfield-shift (2.5–5.8 p.p.m.) of the *beta*-carbon atom, relative to **11**. Remarkable, *gamma*, downfield shifts are observed for C-4 in the 2,6-dideoxy (**13**) and for C-6 in the 4,6-dideoxy derivative (**14**).

On the other hand, in assigning the ^{13}C-n.m.r. resonance-lines of the protected, dideoxy derivatives (**8**, **9**, and **10**), in addition to the effects of the loss of the hydroxyl group, the effects of the substituents have to be taken into account. For **9**, the benzyl groups at HO-2 and HO-4 shift the C-1 signal upfield by 1.9 p.p.m., relative to **12**. The corresponding, upfield shift for **1**, caused by the benzyl groups, is 2.8 p.p.m. For **9**, large downfield-shifts (6–7 p.p.m.) are observed for C-2 and C-4, bearing benzyloxy groups, relative to the free glycoside **12**. For **1**, the corresponding, downfield shifts, relative to **11**, are somewhat larger (7.9–9.2 p.p.m.). Similar downfield-shifts of the ^{13}C-n.m.r. resonance-lines, occurring upon benzylation of the hydroxyl groups, were also found for partially benzylated L-rhamnopyranose derivatives[19]. The shift for C-3 in **9**, relative to that for C-3 in **12** (5.5 p.p.m. upfield), is significantly different from that observed for C-3 in **1**, as compared with **11** (0.1 p.p.m. upfield).

Benzylation of **13** at both HO-3 and HO-4, to give **10**, shifts the resonance of C-2 upfield by 2.0 p.p.m., relative to C-2 in **13**. The corresponding, upfield shift for **2**, relative to **11**, is 2.4 p.p.m. The downfield shift of the C-4 line for **10**, relative to that line for **2** (4.2 p.p.m.), is attributed to the loss of the 1,3-*cis*-diaxial interaction between HO-2 and HO-4 in **2**.

In **8**, the isopropylidene group, and, in methyl 2,3-di-*O*-benzyl-4,6-dideoxy-α-L-*lyxo*-hexopyranoside (**15**), the benzyl groups, shift the C-1 line upfield, relative to **14**. Substitution of the HO-2 and HO-3 groups in **14** with either isopropylidene (**8**) or benzyl groups (**15**) shifts the signals of both C-2 and C-3 to lower field by 4–6 p.p.m. The "alpha" shifts of the isopropylidene group are similar to that of the benzyl group. For **8**, the isopropylidene group has no appreciable effect upon the ^{13}C-n.m.r. chemical-shift of C-4, relative to **14**, whereas benzylation of both HO-2 and HO-3 of **14** causes an upfield shift for C-4 of 1.9 p.p.m. For **8**, the significant upfield-shift of C-5, relative to the chemical shift of that carbon atom in **14** (2.2

p.p.m.), is attributed to the conformational effect of the dioxolane skeleton fused to the pyranoid ring, which distorts the chair conformation of the L-rhamnopyranoside[20]. A similar upfield-shift of C-5 is observed in the ^{13}C-n.m.r. spectrum of **8**, relative to the chemical shift of the corresponding carbon atom in **15**. The *beta*-upfield-shift effect of benzylation is ~2 p.p.m. for the compounds investigated in this study, and was found to be additive (see C-3 in **8** *vs.* C-3 in **12**). For **1**, this effect is cancelled out by the HO-3 group.

For **9**, **10**, and **15**, the range of the upfield *alpha*-shifts caused by the removal of the hydroxyl groups (32.7–42 p.p.m.), relative to the corresponding hydroxylated derivatives, is much broader than that found for the derivatives that have the secondary hydroxyl groups unprotected. Also, the upfield *beta*-shifts cover a broader range (2.1–9.7 p.p.m.).

Inspection of the data in Table II reveals characteristic resonances for the individual, dideoxy derivatives. For **13**, the C-4 line appears at 78.1 p.p.m. This resonance is the lowest-field resonance of all three dideoxyglycosides (except for the resonances corresponding to the anomeric carbon atoms) and, together with the C-2 line at 37.9 p.p.m., and with that for C-1 under 99 p.p.m., may be diagnostic for 2,6-dideoxyaldohexopyranosides. For **14**, the C-5 line appears at 64.3 p.p.m., which is 3.4 p.p.m. higher than the corresponding one for **12** and **13**. For **14**, the C-6 line appears at 21.1 p.p.m., which is the lowest-field resonance found for the C-6 (methyl) atom in this series of unprotected dideoxyaldosides. As, in the ^{13}C-n.m.r. spectra of 4,6-dideoxyaldohexopyranosides (**8**, **14**, and **15**), the positions of the resonance lines corresponding to C-5 and C-6 are only slightly influenced by the substituents on the hydroxyl groups (see Table II), these lines may serve for the identification of 4,6-dideoxyaldohexopyranosides.

The significant, upfield shift for C-6 in **11**, relative to **14** (3.6 p.p.m.), and also that for C-6 in methyl 2,3-di-*O*-benzyl-α-L-rhamnopyranoside, relative to that carbon atom in **15** (3.4 p.p.m.), are attributed to the *γ-gauche*-effect[21] (steric-crowding effect) of the 4-hydroxyl group. For **16**, having a partial structure (HO–C-1–C-2–CH_3 sequence) similar to that in **11**, the *gauche* interactions between the methyl and hydroxyl groups result in a similar upfield-shift (4.2 p.p.m.) of the methyl carbon atom (18.7 p.p.m.: ref. 22), relative to that atom in **17** (22.9 p.p.m.: ref. 22). In the carbohydrate field, a related example was described by Szarek *et al.*[23], who found an upfield shift of 3.9 p.p.m. for C-6 in methyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside, relative to the corresponding signal for methyl 6-chloro-4,6-dideoxy-α-D-*xylo*-hexopyranoside.

The ^{13}C-n.m.r.-spectral characteristics of the title glycosides, as discussed in the foregoing, should contribute to the recognition of these structures in complex, natural compounds, as the effects of a methyl group attached to O-1 of a pyranoside on the ^{13}C-n.m.r. chemical-shifts of the ring-carbon atoms are similar to those of more complex aglycons[24].

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