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Note

^{1}H- and ^{13}C-n.m.r. studies of derivatives of benzyl 2-acetamido-2,6-dideoxy- and 2,4-diacetamido-2,4,6-trideoxy-α-D-gluco- and -galacto-pyranosides*

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The first isolation, in 1959, of a diamino sugar from a bacterial polysaccharide[1,2] and its subsequent identification as 2,4-diacetamido-2,4,6-trideoxy-D-glucose[3–5] prompted our interest in this class of compounds. In the course of our work, a large number of derivatives of 2-acetamido-2,6-dideoxy- and 2,4-diacetamido-2,4,6-trideoxy-D-gluco- and D-galacto-pyranosides was synthesized[4–6]. Of particular significance is the recent identification, in various bacterial polysaccharides[7,8], as well as in a new antibiotic produced by a strain of *Bacillus cereus*[9], of substituted 2,4-diamino-2,4,6-trideoxy-D-galactose, the 2,4-diacetamido analog of which was first prepared synthetically by us[6].

Because of the increasing interest in compounds of this type, we undertook an extensive study of their ^{1}H- and ^{13}C-n.m.r. spectra.

In the present report, we describe n.m.r. studies for solutions (mainly in $CDCl_3$) of nine pairs of α-D-gluco- and α-D-galacto-pyranoside derivatives (described in Scheme 1), where each member of a pair has identical substituents, but differs in its configuration at C-4. The synthesis of five of the compounds (**1b**, **4a**, **4b**, **9a**, and **9b**) is described here for the first time; for the other compounds, see Refs. 5 and 6.

All compounds are assumed to be in the stable $^4C_1$(D) conformation, an assumption considered justified by the absence of a 1,3-*syn*-diaxial interaction between nonhydrogen substituents.

Spectral assignments. — Assignment of the ^{1}H spectra was accomplished by successive homonuclear decoupling. The values of the chemical shifts and the spin–spin coupling constants were originally calculated assuming the spectra to be of first order. The results presented in Tables I and II were determined by comparison

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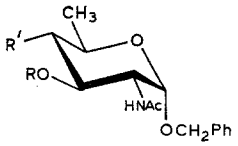

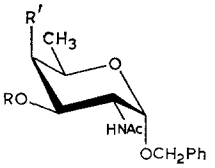

D-*gluco* series	D-*galacto* series	R	R′
1a	**1b**	H	OH
2a	**2b**	H	NHAc
3a	**3b**	Ac	NHAc
4a	**4b**	Ms	NHAc
5a	**5b**	CH_2Ph	NHAc
6a	**6b**	CH_2Ph	OH
7a	**7b**	CH_2Ph	N_3
8a	**8b**	CH_2Ph	OMs
9a	**9b**	CH_2Ph	NHDNP

Scheme 1

TABLE I

VICINAL PROTON–PROTON COUPLING CONSTANTS

Compound	*Coupling constants (Hz)*						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{2,NH}$	$J_{4,NH}$
1a	3.6	10.6	9.1	9.1	6.1		
1b	3.8	10.1	3.2	1.2	6.7		
2a	3.6	9.3	9.6	9.6	5.6	9.3	9.2
2b	3.7	10.9	3.6	~1.2	6.4	8.4	9.1
3a	3.5	10.4	10.4	10.3	6.2	9.6	9.4
3b	3.7	11.5	4.1	~1.2	6.3	9.7	9.1
4a	3.6	10.2	10.2	10.2	6.2	9.4	9.0
4b	3.8	11.1	4.1	~1.2	6.4	9.4	10.3
5a	3.8	10.4	10.4	10.4	6.2	9.2	8.1
5b	3.8	11.2	4.2	~1.2	6.2	8.6	10.1
6a	3.6	10.5	8.8	9.3	6.4	9.1	
6b	3.8	10.8	3.1	~1.2	6.5	9.3	
7a	3.6	10.2	9.4	10.0	6.3	9.4	
7b	3.8	10.2	3.4	~1.2	6.5	8.9	
8a	3.8	10.8	9.5	9.5	6.2	9.6	
8b	3.6	11.0	2.8	~1.2	6.4	9.5	
9a	3.6	9.7	9.8	8.6	6.3	9.6	9.8
9b	3.8	10.3	3.3	~1.2	6.4	8.9	9.2

TABLE II

^{1}H-CHEMICAL SHIFTS IN $CDCl_3$ SOLUTIONS OF SUGAR RING, ALKAMIDE, AND OTHER PROTONS

Compound	*Chemical shifts (p.p.m.)*[a] *Ring protons*					CH_3	*NHAc protons*		CH_3		*Other*
	H-1	*H-2*	*H-3*	*H-4*	*H-5*		*2-NH*	*4-NH*			
1a[b]	4.748	3.911	3.511	3.074	3.635	1.209			1.886		
1b[b]	4.795	4.157	3.660	3.629	3.900	1.211			1.912		
2a	4.777	4.041	3.783	3.673	3.780	1.170			1.954	1.929	
2b	4.909	4.083	3.972	4.323	4.157	1.139	5.750	5.980	2.112	1.984	
3a	4.876	4.346	5.010	3.986	3.724	1.220	5.560	5.280	1.924	1.889	2.008[c]
3b	4.885	4.359	5.137	4.447	4.194	1.109	5.754	6.264	1.991	1.917	2.075[c]
4a	4.907	4.391	4.727	3.978	3.808	1.251	5.851	5.676	2.001	1.957	2.986[d]
4b	4.882	4.499	4.914	4.582	4.153	1.116	5.970	6.868	2.095	1.976	3.069[d]
5a	4.883	4.395	3.866	3.807	3.933	1.219	5.612	5.458	1.920	1.883	
5b	4.917	4.205	3.626	4.626	4.060	1.144	5.432	6.131	2.080	1.932	
6a	4.778	4.193	3.584	3.327	3.743	1.277	6.119		1.813		
6b	4.868	4.495	3.568	3.861	3.901	1.303	5.451		1.882		
7a	4.792	4.270	3.583	3.219	3.635	1.309	5.296		1.799		
7b	4.812	4.438	3.667	3.704	3.863	1.182	5.279		1.803		
8a	4.803	4.395	3.807	4.342	3.928	1.350	5.463		1.821		2.846[d]
8b	4.892	4.517	3.685	5.019	4.030	1.300	5.397		1.905		3.079[d]
9a	4.874	4.417	3.656	3.629	3.929	1.226	5.181		1.890		8.344[e]
9b	4.995	4.398	3.854	4.084	4.274	1.177	5.316		1.832		9.073[e]

[a]Measured from an internal reference of Me_4Si. [b]To increase solubility of these sugars, 10% CD_3OD in $CDCl_3$ was used, leading to an exchange of the NH protons by deuterium. [c]Acetyl methyl group. [d]Methylsulfonyl methyl group. [e]Amino proton of the NHDNP group.

between the experimental and simulated spectra; the latter were obtained by using the Bruker–Panic program. Only limited attempts were made to distinguish between the signals of two identical substituents (for instance, two acetamido groups). Such assignments were accomplished by nuclear Overhauser enhancement (n.O.e.) experiments. Accordingly, the methyl group signals of **3a** at δ 1.889 and 1.924 and of **2b** at δ 1.986 and 2.112 were assigned to the 2- and 4-acetamido groups, respectively.

In the assignments of ^{13}C spectra, we employed the limited data available in the literature, together with such general procedures as selective and off-resonance proton decoupling. Furthermore, the measurement of related compounds provided, in several cases, great help in the assignments.

The signals of substituent groups in ^{13}C spectra usually appear quite remote from those of the pyranose-ring atoms and can therefore be assigned readily on the basis of published data. Accordingly, we assigned the resonances in the δ 170–180 region to the carbonyl groups of the acetamido and acetoxyl groups, and those at δ 137 and 128 to the phenyl groups. The methyl group of the methylsulfonyl (mesyl), acetamido, and acetoxyl groups resonates at δ 30, 23, and 20, respectively. Assignment of the methylene carbon atoms of the benzyl group at δ 70 was, in several cases,

TABLE III

^{13}C CHEMICAL SHIFTS IN $CDCl_3$ SOLUTION OF THE CARBON ATOMS OF THE SUGAR RING AND OF THE C-5 METHYL GROUP.

Compound	*Chemical shift (p.p.m.)*[a]					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*CH_3*
1a[b]	96.94	53.79	76.82	76.50	68.05	17.58
1b[b]	97.25	50.27	69.86	71.68	66.69	16.33
2a	97.00	54.59	69.82	57.84	67.38	17.94
2b	97.15	50.69	68.06	53.79	65.39	16.64
3a	96.82	51.83	69.70	55.08	67.73	17.78
3b	97.05	48.12	69.43	50.77	65.06	16.46
4a	96.80	51.84	77.87	54.99	67.43	17.43
4b	97.31	48.00	76.20	51.60	65.11	16.24
5a	97.34	51.84	76.62	55.84	67.48	17.90
5b	97.33	49.36	74.65	49.65	65.60	16.82
6a	97.31	52.30	80.49	75.62	68.02	17.64
6b	97.57	47.95	76.81	68.54	66.07	16.45
7a	97.22	52.47	78.84	68.43	67.00	18.45
7b	97.33	48.50	76.71	63.08	65.05	17.54
8a	96.95	52.89	78.16	83.29	66.51	17.64
8b	97.45	48.14	74.02	79.41	65.98	16.73
9a	97.25	53.13	80.64	60.67	67.43	18.12
9b	97.29	49.13	73.63	56.22	65.32	16.96

[a]Measured from an internal reference of Me_4Si. [b]To increase solubility of these sugars, 10% CD_3OD in $CDCl_3$ was used.

difficult because of the presence of signals of the pyranose ring carbons in this region of the spectra. However, these signals could be identified on the basis of the coupled spectra.

Among the ring-carbon resonances, that of C-1 was readily identified as it is known to appear at low field (δ 90–100), and is almost independent of the configuration at C-4 or of the nature of the substituents at C-3 and C-4. The signal of C-2 in both the *gluco* and *galacto* compounds **1** and **6–9** could be readily identified by the relative high-field shift (at δ 50) arising from the presence of the 2-acetamido group[11]. In compounds **2–5** having two acetamido groups, two upfield-shifted signals (also at δ 50) were observed. The distinction between them is rather difficult and was accomplished in several cases only by selective proton-decoupling, provided that the H-2 and -4 signals were separated.

The coupling constants and chemical shifts of the compounds examined are presented in Tables I–III.

Effect of epimerization at C-4 on n.m.r. data. — The vicinal-proton coupling-constants $J_{3,4}$ and $J_{4,5}$, lie in the expected range for all compounds examined, being high for the *gluco* ($J_{3,4}$ and $J_{4,5}$ ~10 Hz) and low for the *galacto* derivatives ($J_{3,4}$ ~4, $J_{4,5}$ ~1 Hz).

The H-4 resonance shifts towards lower field upon epimerization of the *gluco* to the corresponding *galacto* derivatives, which is in accordance with the rule of Lemieux[12], and with other published data on substituted cyclohexanes, that axially oriented protons are more shielded than equatorial ones. It may be seen, further, from the experimental data, that the epimerization is associated with a relatively large deshielding of H-5 and of the NH group of 4-NHAc. The direction of shift of the H-3 signal is irregular, and in some cases in the opposite direction from that observed by Lemieux and Stevens[13]. The shifts of the signals of H-1, H-2, and the C-6 methyl protons are small (within 0.1 p.p.m.) and irregular, except in compounds having OH-3, where shifts of up to 0.3 p.p.m. are observed for H-2. As may be seen from Table II, the shifts of H-4 and -5 signals resulting from epimerization at C-4 are strongly influenced by the substituents at C-4 and -3.

The epimerization also affects the chemical shifts of the substituents. The methyl groups of the acetamido and/or the mesyl substituents are shifted, to a very small extent, toward lower field as a result of the change in configuration at C-4. Of a special interest are the relatively large downfield shifts ($\sim$1 p.p.m.) of the amide protons of the acetamido groups at position 4 observed for the *galacto* derivatives (compounds **3**, **4**, and **5**). These shifts arise most probably from interaction between the amide proton and the ring oxygen atom in the *galacto* derivatives, a factor absent in the *gluco* derivatives. The methylene resonance of the benzyl group in compounds having one benzyl group (at O-1) is scarcely affected by the epimerization. On the other hand, in compounds having two benzyl groups (at O-1 and O-3) the methylene resonance of one of the benzyl groups (most probably that at O-3) is affected by epimerization.

The upfield shifts of the ^{13}C resonances of C-2 (2.5–4.5 p.p.m.) and C-5 (0.5–2.5 p.p.m.) resulting from epimerization at C-4 may be explained in terms of established rules of ^{13}C-n.m.r. spectroscopy[14], as well as from published ^{13}C-n.m.r. data of sugars[10].

The upfield shifts of C-4 following epimerization are in agreement with published ^{13}C-n.m.r. data on cyclohexane derivatives and on the interconversion at C-1 in which the reorientation of a substituent group from axial to equatorial is associated with deshielding (experimental values are 7–4 p.p.m.). Further inspection of the results reveals that both the C-3 and the C-6 signals are also shifted upfield as a result of epimerization at C-4, which is also in agreement with data given for monosubstituted cyclohexane derivatives[14].

Spin–spin coupling-constants. — The measured values of the vicinal proton–proton coupling constants between axial and equatorial pairs of protons are $J_{1,2}$ 3.5–3.8 Hz for both the *gluco* and the *galacto* epimers, and $J_{3,4}$ 2.8–4.2 and $J_{4,5}$ $\sim$1.2 Hz for the *galacto* epimer. The various J values may be characterized in terms of the empirical rules suggested by de Bruyn and Anteunis[15], and are in good agreement with the additivity rule for pyranose rings proposed by Altona and Haasnoot[16]. The assumption that the compounds examined are all in the stable $^4C_1$ conformation is therefore fully justified.

Chemical shifts. — The effect of substitution of an hydroxyl group by other groups, on the chemical shifts of the sugar ring protons and carbon atoms, may be deduced from the data in Tables II and III. However, because the compounds studied by us are highly substituted with bulky groups, it is possible that part of the observed shifts, especially in the β and γ positions, may result from changes in the averaged conformation of neighboring substituent-groups. We shall, therefore, consider the effect of substitution on the chemical shifts only in the α position. Thus, the introduction of a mesyl group at C-3 and C-4 causes deshielding of 1 and 9 p.p.m., respectively, of the α proton and carbon atom, and is almost independent of the neighboring substituent groups. Substitution by a dinitroanilino group is associated with a 0.3-p.p.m. downfield shift of the α proton, while the α carbon atom shifts 10 p.p.m. toward higher field. As a result of replacement of OH by an azide group, the α carbon atom shifts 7 p.p.m. upfield, whereas the chemical shift of the α proton is hardly affected.

The observed chemical shifts of the sugar protons and carbon atoms arising from substitution by AcO and NHAc groups are in agreement with previously published data[10].

EXPERIMENTAL

General methods. — Melting points were measured in capillary tubes on a Büchi apparatus and are not corrected. Optical rotations were determined in chloroform (*c* 0.5) with a Bendix ETL-NPL polarimeter. N.m.r. spectra were recorded with Bruker WH-90 (22.63 MHz for the ^{13}C measurements) and Bruker WH-270 (270 MHz for the ^{1}H measurements) spectrometers operating in the Fourier-transform mode with tetramethylsilane as the internal standard and usually chloroform-*d* as solvent. Columns were prepared with silica gel (E. Merck, No. 7734) and t.l.c. was performed with silica gel-coated aluminum sheets (E. Merck). Chromatograms were sprayed with dilute sulfuric acid. Evaporations were conducted *in vacuo*.

Benzyl 2-acetamido-2,6-dideoxy-α-D-galactopyranoside (**1b**). — A solution of benzyl 2-acetamido-3-*O*-benzyl-2,6-dideoxy-α-D-galactopyranoside[5] (1.0 g) in methanol (300 mL) was hydrogenolyzed in the presence of 10% palladium-on-charcoal (0.4 g) for 24 h at room temperature. The catalyst was removed by filtration and the filtrate evaporated. The residue was dissolved in a small amount of abs. ethanol, the ethanol evaporated, and the resulting product redissolved in ethanol. Addition of an excess of petroleum ether gave a precipitate that was collected by centrifugation and dried *in vacuo*. The dried residue (0.70 g) was fractionated on a column (60 g) of silica gel pre-equilibrated with 6:2 (v/v) chloroform–ethanol and the title product eluted with the same solvent as a single, homogeneous fraction, [t.l.c., R_F 0.8 in 3:1 (v/v) chloroform–ethanol]. It was recrystallized from abs. ethanol–petroleum ether; yield 0.35 g (50%), m.p. 210°, $[\alpha]_D^{22}$ +153° (*c* 0.5, chloroform).

Anal. Calc. for $C_{15}H_{21}NO_5$: C, 61.00; H, 7.17; N, 4.75. Found: C, 60.98; H, 7.23; N, 4.75.

Benzyl 2,4-diacetamido-2,4,6-trideoxy-3-O-(methylsulfonyl)-α-D-glucopyranoside (**4a**). — To a solution of benzyl 2,4-diacetamido-2,4,6-trideoxy-α-D-glucopyranoside[6] (0.17 g in 12 mL of abs. pyridine), cooled to 2° in an ice bath was added dropwise 0.25 mL of methanesulfonyl chloride during 0.5 h, with constant stirring. Stirring was continued in the cold for another 1.5 h, and then for 3 h at room temperature. Ice was then added to the mixture, which was extracted with several portions of chloroform (total volume 400 mL). The extract was washed with water (2 × 150 mL), and then with saturated sodium chloride (100 mL), and was dried over sodium sulfate. The chloroform was evaporated. To remove the pyridine, the residue was suspended in 1:1 (v/v) toluene–ethanol (150 mL) and the solvent removed by evaporation. This procedure was repeated twice. The residue was boiled under reflux in chloroform (300 mL) containing 0.5 g of charcoal. The charcoal was removed by filtration, the chloroform evaporated, abs. ethanol and abs. ether (1:1) were added, and the solvent was removed by evaporation. Upon trituration of the dried residue in absolute petroleum ether, complete crystallization occurred. The crystalline product was kept overnight in the cold, and then collected by filtration and dried in a desiccator; yield 0.14 g (67%); m.p. 195–196°, $[\alpha]_D^{22}$ +121°.

Anal. Calc. for $C_{18}H_{26}N_2O_7S$: C, 52.17; H, 6.32; N, 6.76. Found: C, 52.17; H, 6.33. N, 6.75.

Benzyl 2,4-diacetamido-2,4,6-trideoxy-3-O-(methylsulfonyl)-α-D-galactopyranoside (**4b**). — Benzyl 2,4-diacetamido-2,4,6-trideoxy-α-D-galactopyranoside[7] (0.3 g) was dissolved with heating in abs. pyridine (10 mL) and treated with methanesulfonyl chloride (0.45 mL) as described for synthesis of the gluco analog. The crude product was isolated by extraction with chloroform, and the extract treated as described. After decolorization with charcoal and evaporation of the chloroform, an oil was obtained that was dissolved in chloroform (15 mL), and an excess of petroleum ether was added. The white precipitate formed was collected by filtration, washed with petroleum ether, and dried in a desiccator, yield 0.25 g (68%), m.p. 120°, $[\alpha]_D^{22}$ +116.5°. The product migrated as a single spot in t.l.c. (R_F 0.56 in 6:2 chloroform–methanol).

Anal. Calc. for $C_{18}H_{26}N_2O_7S$: C, 52.17; H, 6.32; N, 6.76. Found: C, 52.17; H, 6.33; N, 6.75.

Benzyl 2-acetamido-4-amino-3-O-benzyl-2,4,6-trideoxy-α-D-galactopyranoside. — Benzyl 2-acetamido-4-azido-3-*O*-benzyl-2,4,6-trideoxy-α-D-galactopyranoside[6] (1.5 g) in methanol (450 mL) was hydrogenated at atmospheric pressure in the presence of 10% palladium-on-charcoal catalyst (0.7 g) for 6 h. The catalyst was filtered off and washed with methanol. The methanol was removed by evaporation, the residue dissolved in abs. methanol, and the solvent evaporated off. This procedure was repeated. Trituration with petroleum ether gave crystals, which were kept overnight. The crystalline material was then collected by filtration to give the title product, which melted at 150°, and then solidified, and melted again at 180°; yield 1.2 g (88%); $[\alpha]_D^{22}$ +166.6°.

Anal. Calc. for $C_{22}H_{28}N_2O_4$: C, 68.72; H, 7.34; N, 7.29. Found: C, 68.60; H, 7.29; N, 7.30.

Benzyl 2-acetamido-3-O-benzyl-2,4,6-trideoxy-4-(2,4-dinitroanilino)-α-D-galactopyranoside (**9b**). — Benzyl 2-acetamido-4-amino-3-*O*-benzyl-2,4,6-trideoxy-α-D-galactopyranoside (1.2 g) was dissolved with heating in 3.3% sodium hydrogencarbonate (15 mL) and ethanol (15 mL) was added, followed by a solution of 1-fluoro-2,4-dinitrobenzene (1 mL) in ethanol (15 mL). After shaking for 3 h at room temperature in the dark, the solution was evaporated and the residue extracted with chloroform (1 L). The extract was washed extensively with M sodium hydroxide (7 L), and then with water to neutrality, and dried over sodium sulfate. The chloroform was evaporated off and the residue washed with abs. ether to remove traces of 1-fluoro-2,4-dinitrobenzene. Upon drying *in vacuo*, 1.2 g of the crude title product was obtained, migrating in t.l.c. (chloroform) as a single yellow spot (R_F 0.25). Recrystallization from 1 L of 7:4 (v/v) ethanol–water gave fine needles which were collected by filtration and dried *in vacuo*; yield 0.95 g (55%); m.p. 190–191°, $[\alpha]_D^{22}$ +297.4°.

Anal. Calc. for $C_{28}H_{30}N_4O_8$: C, 61.09; H, 5.49; N, 10.17. Found: C, 61.24; H, 5.47; N, 10.17.

Benzyl 2-acetamido-3-O-benzyl-4-(2,4-dinitroanilino)-α-D-glucopyranoside (**9a**). — This compound was prepared from benzyl 2-acetamido-4-azido-2,4,6-trideoxy-α-D-glucopyranoside[5] *via* the 4-amine (yield 74%) as described for the galacto analog (**9b**), except that the 4-amine was not fully characterized. The crystalline product migrated as a single spot in t.l.c. in chloroform (R_F 0.25) yield 0.35 g (31%, based on the 4-amine); m.p. 192–193°, $[\alpha]_D^{22}$ +9.4°.

Anal. Calc. for $C_{28}H_{30}N_4O_8$: C, 61.09; H, 5.49; N, 10.17. Found: C, 61.00; H, 5.40; N, 10.11.

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