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Syntheses of 2,6-anhydroaldonic acids from the corresponding anhydrodeoxynitroalditols (glycopyranosylnitromethanes) and their conversion into methyl esters, amides, and alditols

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Abstract

2,6-Anhydroaldonic acids were obtained by oxidation of the corresponding anhydrodeoxynitroalditols (glycopyranosylnitromethanes) with hydrogen peroxide in alkaline solution. Purification was achieved via the methyl anhydroaldonates. The syntheses of five 2,6-anhydrohexonic and eight 2,6-anhydroheptonic acids were accomplished in yields of 44–81%. All corresponding unprotected and acetylated methyl 2,6-anhydroaldonates were characterised. Ammonolysis of the former afforded the corresponding amides in quantitative yields; reduction with sodium borohydride gave the analogous anhydroalditols.

Keywords: 2,6-Anhydroaldonic acids; Methyl 2,6-anhydroaldonates; 2,6-Anhydroaldonamides; Anhydroalditols; Anhydrodeoxynitroalditols

1. Introduction

The classical route to 2,6-anhydroaldonic acids was introduced by Helferich and co-workers [1] and involves conversion of *O*-protected glycopyranosyl bromides with mercury(II) cyanide into the corresponding nitriles (glycopyranosyl cyanides) [2] which are converted into the methyl esters and sodium salts of the acids [1]. The isolation of the corresponding free acids was reported 4 years later by Fuchs and Lehmann [3]. With the use of trimethylsilyl cyanide, the toxicological problems associated with mercury can be avoided and glycopyranose peracetates can be employed directly with a Lewis acid as catalyst [4]. Nevertheless, because of the formation of mixed anomers and undesired by-products, these methods cannot be considered as universally applicable for the synthesis of 2,6-anhydroaldonic acids and their derivatives.

A highly efficient alternative method has been developed in this laboratory [5]. It involves the following steps: cyclodehydration [6] of the nitroalditols obtained by the addition of nitromethane

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to aldoses (Fischer–Sowden reaction [7]) and subsequent acetylation of the resultant anhydrodeoxynitroalditols (glycopyranosylnitromethanes). Treatment of these acetates with phosphorus trichloride in pyridine yields the fully acetylated glycopyranosyl cyanides very efficiently [5], and these can be hydrolysed to 2,6-anhydroaldonic acids [1,3].

In the present paper we report on a more-direct route to these acids which also starts from glycopyranosylnitromethanes and uses hydrogen peroxide as an oxidising agent.

2. Results and discussion

In 1974, Bílik [8] reported that addition of hydrogen peroxide to aqueous (and thus alkaline) solutions of sodium salts of 1-deoxy-1-nitroalditols in the presence of catalytic amounts of molybdate, tungstate, or vanadate anions led exclusively to the aldoses formed similarly in a Nef reaction [9]. The latter, by contrast, requires strong acidic reaction conditions. It was stated explicitly that the catalyst is essential for this alternative approach to higher aldoses, which circumvents the intricacies of the Nef reaction. Later on [10] it was found that a reaction, formally constituting a retro-nitromethane addition, competes at high pH.

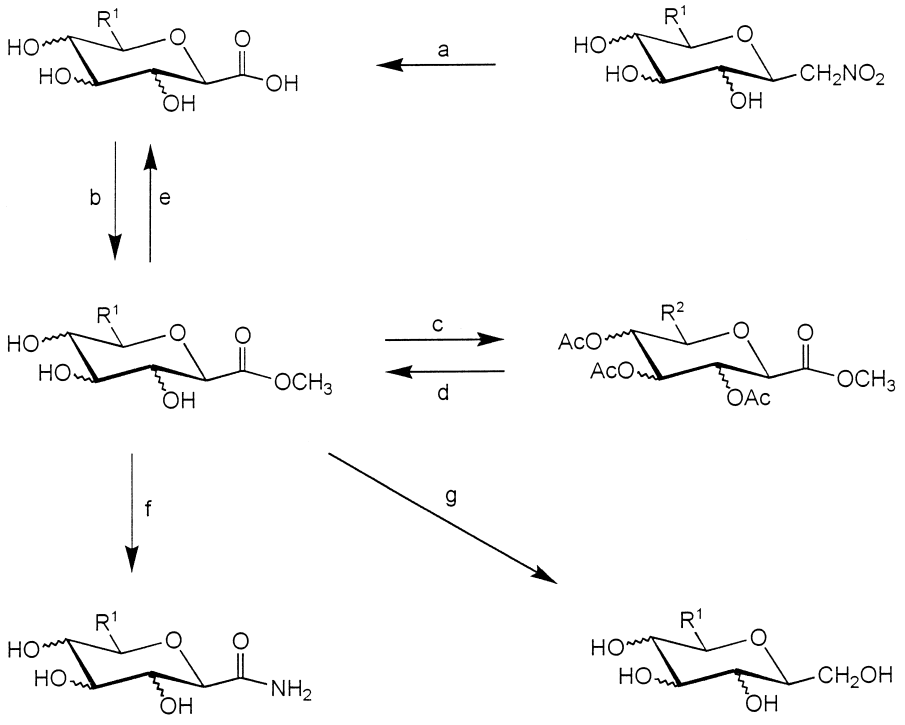
In 1980, Olah et al. [11] reported more generally on the transformation of primary and secondary nitroalkanes into aldehydes and ketones, respectively, in yields between 76 and 96% by treatment with hydrogen peroxide (30%) in methanol–water in the presence of potassium carbonate. We applied these reaction conditions, which do not demand contamination of the reaction mixture by a catalyst, to the readily available deoxynitroalditols and their 2,6-anhydrides, with the objective of preparing aldoses and anhydroaldoses, in spite of the aforementioned statements of the previous authors [8,10].

By oxidation of acyclic nitroalditols with hydrogen peroxide in aqueous potassium carbonate (pH ~14) for the reaction times given in the literature procedure [11], the aldoses derived by loss of C-1 were produced and completely degraded within several days [unpublished results]. However, when the reaction was carried out near pH 9 (sodium hydrogencarbonate), aldoses were produced by oxidative loss of the nitro group as in the Nef reaction, together with high proportions of the lower aldoses formed by loss of C-1 [unpublished results]. Only these cases resemble the Bílik reaction [8] just mentioned. At pH values below 8, no reaction occurred.

In the case of the anhydronitroalditols, entirely different results were obtained. Furanoid anhydrodeoxynitroalditols (glycofuranosylnitromethanes) generally underwent severe decomposition on treatment with hydrogen peroxide in alkaline media, and consequently these routes were not followed any further.

In contrast, pyranoid anhydrodeoxynitroalditols (glycopyranosylnitromethanes) [6], being more stable, when treated with hydrogen peroxide in aqueous potassium carbonate (pH ~14) at 20 °C underwent conversion into the corresponding 2,6-anhydroaldonic acids [12,13]. Although most of the starting material had already been consumed after 16 h, prolongation of the reaction times from 48 up to 72 h afforded almost quantitative yields. Removal of the potassium cations with exchange resin and treatment of the crude residues obtained by evaporation of the solvents with boiling dry methanol led to the corresponding methyl esters under the influence of the residual nitric acid. Two general routes (A and B) for the purification of the acids are outlined in Scheme 1. Route A (steps a–b–c–d–e) involved acetylation of the crude methyl esters with acetic anhydride in pyridine and separation of the acetates by chromatography on silica gel. Deacetylation [14] and saponification, followed by acidification, gave the free aldonic acids. Route B (steps a–b–e) is more direct, but requires more sophisticated chromatographic equipment for the purification of the unprotected methyl esters.

Four pyranoid anhydrodeoxynitrohexitols (*β*-glycopyranosylnitromethanes, derived from the pentoses L-arabinose, D-lyxose, D-ribose, and D-xylose) and eight 2,6-anhydrodeoxynitroheptitols (*β*-glycopyranosylnitromethanes, derived from the eight D-hexoses), each bearing an equatorial nitromethyl group [6], were oxidised and the crude 2,6-anhydroaldonic acids were purified by the foregoing procedures. In addition, 2,6-anhydro-D-*altro*-hexonic acid (**13a**, Table 1, derived from 2,6-anhydro-1-deoxy-1-nitro-D-*altro*-hexitol [13,15]), the *α* anomer of 2,6-anhydro-D-*allo*-hexonic acid (**3b**), and its esters were synthesised because of the ready availability of compounds having this configuration. In contrast to the other compounds studied, all of which have the *β*-configuration at



R^1 = H, CH_2OH; R^2 = H, CH_2OAc
Route A via steps a-b-c-d-e; **Route B** via steps a-b-e

Scheme 1. (a) H_2O_2 (30%, aq), K_2CO_3, 20 °C, 48–72 h; (b) dry MeOH, HNO_3, reflux, 16 h; (c) Ac_2O, pyridine, 20 °C, 6–16 h; (d) NaOMe, dry MeOH, 20 °C, 1 h; (e) NaOH (0.5 N, aq), 60 °C, 2 h, then Amberlite IR-120 (H^+); (f) NH_3, MeOH, 5 °C, 6 h; (g) $NaBH_4$ (0.3 M, aq), Amberlite IR-120 (H^+), 0–5 °C, 12 h.

C-2 and adopt the $^5C_2$ conformation, **13a** and its derivatives have the α-configuration at C-2 and adopt the $^2C_5$ conformation. All of the compounds described therefore have the carboxyl groups in the thermodynamically favourable equatorial positions.

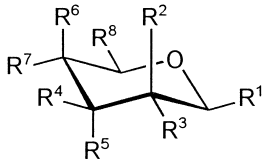
By treating the methyl 2,6-anhydroaldonates with cold saturated ammoniacal methanol the corresponding 2,6-anhydroaldonamides were obtained in quantitative yields. This reaction can also be applied to the per-*O*-acetylated methyl esters, but reaction of ammonia with the acetate groups yielded acetamide, which was difficult to separate from the desired products by fractional crystallisation. Therefore, although the 2,6-anhydroaldonic acid amides could be isolated by chromatographic methods, it is more convenient to deacetylate the protected methyl esters before ammonolysis.

On reduction of methyl 2,6-anhydroaldonates **4b** [16], **7b** [3,17,18], **8b** [3,19], and **11b** [19,20] by a modified Wolfrom and Thompson procedure [21] with aqueous sodium borohydride in the presence of cationic exchange resin, the corresponding anhydroalditols 1,5-anhydro-L-*gluco*-hexitol (**4e**) [22], 2,6-anhydro-L-*glycero*-L-*galacto*-heptitol (**7e**, described previously [18,23] as 2,6-anhydro-D-*glycero*-L-*manno*-heptitol), the *meso* compound 2,6-anhydro-*meso*-D-*glycero*-D-*gulo*-heptitol (**8e**) [24,25,26], and 2,6-anhydro-D-*glycero*-D-*galacto*-heptitol (**11e**, the enantiomer of **7e**) [27,28] were obtained in yields greater than 90%.

Table 1 gives a survey of all compounds prepared. Their structures were confirmed by NMR data, which are summarised in Tables 2–4.

The chemical-ionisation mass spectroscopy (CIMS) fragmentation patterns (Table 5) of the hydroxy acids (**a** series) and hydroxy esters (**b** series) were characterised by loss of the C-2 substituents ($[M+H]^+-ROH$ and $[M+H]^+-ROH-CO$ with R = H or Me) followed sequentially by the loss of two water molecules, and are thus analogous to those of the free aldoses [29,30]. Because of the formal loss of formaldehyde at the primary hydroxy group, the anhydroheptonic acids showed also the fragments found for their hexonic analogues. The *O*-acetylated methyl esters (**c** series), in

Table 1
2,6-Anhydroaldonic acids, their OH-free and fully *O*-acetylated methyl esters, their amides and four anhydroalditols



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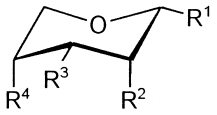

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Compound	Configuration	Derived from	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	Route	Yield%
1a	L-*manno*	L-arabinose	CO_2H	H	OH	OH	H	OH	H	H	A	57[a]
1b [17]	L-*manno*	L-arabinose	CO_2Me	H	OH	OH	H	OH	H	H	A	71[a]
1c	L-*manno*	L-arabinose	CO_2Me	H	OAc	OAc	H	OAc	H	H	A	87[a]
1d	L-*manno*	L-arabinose	$CONH_2$	H	OH	OH	H	OH	H	H	c	98[b]
2a	D-*galacto*	D-lyxose	CO_2H	OH	H	OH	H	H	OH	H	B	64[a]
2b	D-*galacto*	D-lyxose	CO_2Me	OH	H	OH	H	H	OH	H	B	70[a]
2c	D-*galacto*	D-lyxose	CO_2Me	OAc	H	OAc	H	H	OAc	H	B	91[a]
2d	D-*galacto*	D-lyxose	$CONH_2$	OH	H	OH	H	H	OH	H	c	93[b]
3a	D-*allo*	D-ribose	CO_2H	H	OH	H	OH	H	OH	H	B	59[a]
3b	D-*allo*	D-ribose	CO_2Me	H	OH	H	OH	H	OH	H	B	87[a]
3c	D-*allo*	D-ribose	CO_2Me	H	OAc	H	OAc	H	OAc	H	B	71[a]
3d	D-*allo*	D-ribose	$CONH_2$	H	OH	H	OH	H	OH	H	c	98[b]
4a	D-*gulo*	D-xylose	CO_2H	H	OH	OH	H	H	OH	H	A	50[a]
4b [16]	D-*gulo*	D-xylose	CO_2Me	H	OH	OH	H	H	OH	H	A	70[a]
4c	D-*gulo*	D-xylose	CO_2Me	H	OAc	OAc	H	H	OAc	H	A	91[a]
4d	D-*gulo*	D-xylose	$CONH_2$	H	OH	OH	H	H	OH	H	c	95[b]
4e	L-*gluco*	D-xylose	CH_2OH	H	OH	OH	H	H	OH	H	d	90[b]
5a	D-*glycero*-D-*allo*	D-allose	CO_2H	H	OH	H	OH	H	OH	CH_2OH	B	59[a]
5b	D-*glycero*-D-*allo*	D-allose	CO_2Me	H	OH	H	OH	H	OH	CH_2OH	B	78[a]
5c	D-*glycero*-D-*allo*	D-allose	CO_2Me	H	OAc	H	OAc	H	OAc	CH_2OAc	B	73[a]
5d	D-*glycero*-D-*allo*	D-allose	$CONH_2$	H	OH	H	OH	H	OH	CH_2OH	c	87[b]
6a	D-*glycero*-D-*gluco*	D-altrose	CO_2H	OH	H	H	OH	H	OH	CH_2OH	A	44[a]
6b	D-*glycero*-D-*gluco*	D-altrose	CO_2Me	OH	H	H	OH	H	OH	CH_2OH	A	71[a]
6c	D-*glycero*-D-*gluco*	D-altrose	CO_2Me	OAc	H	H	OAc	H	OAc	CH_2OAc	A	91[a]
6d	D-*glycero*-D-*gluco*	D-altrose	$CONH_2$	OH	H	H	OH	H	OH	CH_2OH	c	93[b]
7a [3,17]	D-*glycero*-L-*manno*	D-galactose	CO_2H	H	OH	OH	H	OH	H	CH_2OH	A	54[a]
7b [3,17,18]	D-*glycero*-L-*manno*	D-galactose	CO_2Me	H	OH	OH	H	OH	H	CH_2OH	A	74[a]
7c	D-*glycero*-L-*manno*	D-galactose	CO_2Me	H	OAc	OAc	H	OAc	H	CH_2OAc	A	90[a]
7d [18]	D-*glycero*-L-*manno*	D-galactose	$CONH_2$	H	OH	OH	H	OH	H	CH_2OH	c	92[b]
7e [18,23]	L-*glycero*-L-*galacto*	D-galactose	CH_2OH	H	OH	OH	H	OH	H	CH_2OH	d	86[b]
8a [3,19,26]	D-*glycero*-D-*gulo*	D-glucose	CO_2H	H	OH	OH	H	H	OH	CH_2OH	A	62[a]
8b [3,19]	D-*glycero*-D-*gulo*	D-glucose	CO_2Me	H	OH	OH	H	H	OH	CH_2OH	A	75[a]
8c [1,19,26,31]	D-*glycero*-D-*gulo*	D-glucose	CO_2Me	H	OAc	OAc	H	H	OAc	CH_2OAc	A	87[a]
8d	D-*glycero*-D-*gulo*	D-glucose	$CONH_2$	H	OH	OH	H	H	OH	CH_2OH	c	86[b]
8e [24–26]	D-*glycero*-D-*gulo*	D-glucose	CH_2OH	H	OH	OH	H	H	OH	CH_2OH	d	89[b]
9a	D-*glycero*-L-*talo*	D-gulose	CO_2H	H	OH	H	OH	OH	H	CH_2OH	A	75[a]
9b	D-*glycero*-L-*talo*	D-gulose	CO_2Me	H	OH	H	OH	OH	H	CH_2OH	A	78[a]
9c	D-*glycero*-L-*talo*	D-gulose	CO_2Me	H	OAc	H	OAc	OAc	H	CH_2OAc	A	99[a]
9d	D-*glycero*-L-*talo*	D-gulose	$CONH_2$	H	OH	H	OH	OH	H	CH_2OH	c	96[b]
10a	D-*glycero*-L-*ido*	D-idose	CO_2H	OH	H	H	OH	OH	H	CH_2OH	B	81[a]
10b	D-*glycero*-L-*ido*	D-idose	CO_2Me	OH	H	H	OH	OH	H	CH_2OH	B	79[a]
10c	D-*glycero*-L-*ido*	D-idose	CO_2Me	OAc	H	H	OAc	OAc	H	CH_2OAc	B	82[a]
10d	D-*glycero*-L-*ido*	D-idose	$CONH_2$	OH	H	H	OH	OH	H	CH_2OH	c	99[b]
11a	D-*glycero*-D-*galacto*	D-mannose	CO_2H	OH	H	OH	H	H	OH	CH_2OH	B	75[a]
11b [19,20]	D-*glycero*-D-*galacto*	D-mannose	CO_2Me	OH	H	OH	H	H	OH	CH_2OH	B	87[a]
11c [19,32]	D-*glycero*-D-*galacto*	D-mannose	CO_2Me	OAc	H	OAc	H	H	OAc	CH_2OAc	B	86[a]
11d	D-*glycero*-D-*galacto*	D-mannose	$CONH_2$	OH	H	OH	H	H	OH	CH_2OH	c	91[b]
11e [27,28]	D-*glycero*-D-*galacto*	D-mannose	CH_2OH	OH	H	OH	H	H	OH	CH_2OH	d	87[b]
12a	D-*glycero*-L-*altro*	D-talose	CO_2H	OH	H	OH	H	OH	H	CH_2OH	B	65[a]
12b	D-*glycero*-L-*altro*	D-talose	CO_2Me	OH	H	OH	H	OH	H	CH_2OH	B	85[a]
12c [32]	D-*glycero*-L-*altro*	D-talose	CO_2Me	OAc	H	OAc	H	OAc	H	CH_2OAc	B	77[a]

(continued)

Table 1—*contd*

12d	D-*glycero*-L-*altro*	D-talose	$CONH_2$	OH	H	OH	H	OH	H	CH_2OH	c	92[b]
13a	D-*altro*	D-ribose	CO_2H	OH	OH	OH	—	—	—	—	e	60[a]
13b	D-*altro*	D-ribose	CO_2Me	OH	OH	OH	—	—	—	—	e	48[a]
13c	D-*altro*	D-ribose	CO_2Me	OAc	OAc	OAc	—	—	—	—	e	31[a]
13d	D-*altro*	D-ribose	$CONH_2$	OH	OH	OH	—	—	—	—	c	100[b]

[a] Based on the corresponding anhydrodeoxynitroalditol.
[b] Based on the corresponding methyl anhydroaldonate.
[c] Ammonolysis of the corresponding methyl anhydroaldonate.
[d] Reduction of the corresponding methyl anhydroaldonate.
[e] Direct crystallisation.

parallel manner, lost the C-2 substituents and then two molecules of acetic acid and ketene. They, therefore, show analogous fragmentation paths to those of the acetylated aldopyranoses [29]. In addition, fragmentation of the protonated dimers $[2M+H]^+$ could be observed. Fragmentation was not detected in the cases of the amides (**d** series), only the $[M+H]^+$ and $[2M+H]^+$ species being observed. The fragmentation of the anhydroalditols was exclusively characterised by the loss of water.

In order to obtain a complete set of data, the IR spectra from the crystalline unprotected compounds and all fully *O*-acetylated methyl esters were determined. Because of the similarity of the compounds it seemed necessary for us to list the significant peaks, even in the fingerprint region.

3. Experimental

General methods.—All solvents used for reactions were distilled before use. The progress of reactions was observed by TLC (Merck, silica gel F_{254}), with detection by charring with H_2SO_4 (10%). Column chromatography was performed on silica gel 60 (Merck, 63–200 μm). For TLC and column chromatography the following solvent systems (*s.s.*) were used (v/v): *s.s.* 1, 7:7:6:2:2 EtOAc–EtOH–AcOH (50%)–MeOH–*n*-BuOAc; *s.s.* 2, 10:1 *tert*-BuOMe–petroleum ether (PE) (40/60); *s.s.* 3, 5:3:1 EtOAc–MeOH–toluene; *s.s.* 4, 1:1 EtOAc–PE (60–80); *s.s.* 5, 2:1 EtOAc–PE (60–80); *s.s.* 6, 3:1 EtOAc–PE (60–80); *s.s.* 7, 19:1 CH_2Cl_2–Me_2CO. Amberlite IR-120 (H^+-form) cation-exchange resin and Amberlite IRA-400 (HCO_3^--form) anion-exchange resin were employed for deionisations. Melting points were determined on the heating table of a Leitz Laborlux 12 microscope and are uncorrected. Optical rotations were measured at 20 °C with a Perkin–Elmer 241 MC polarimeter. The samples were dissolved 24 h before measurements to allow equilibrations. The concentrations of all samples were 1% (w/v). Hydroxylic compounds were measured in H_2O, acetylated esters in $CDCl_3$. Elemental analyses were carried out by use of an Erba-Science analyser, model 1104. The ^1H (500.13 MHz) and ^{13}C (125.75 MHz) NMR spectra were recorded with a Bruker AMX R500 spectrometer. The assignment of signals of the carbon atoms was done by ^1H–^{13}C correlated 2D-spectroscopy using the software "INVCH". The correlation of the hydrogen atoms was done in cases of doubt by ^1H–^1H correlated spectra with the program "COSYHH". All ^1H NMR spectra measured in D_2O were referred to internal Me_2CO (^1H δ 2.09, ^{13}C δ 30.5). All samples measured in $CDCl_3$ refer to internal $CHCl_3$ [δ 7.24 or 77.0 (middle signal of the $CDCl_3$-triplet), respectively]. IR spectra were recorded on a Philips PU 9706 spectrometer. Crystalline samples were incorporated in KBr pellets. Syrupy compounds were dissolved in CCl_4 and held between NaCl monocrystalline plates. The measurements of the chemical-ionisation mass spectra (CIMS) were carried out on a Finnigan MAT 95 including the data system DEC 5000. Crystalline samples were applied directly onto the target, syrups were dissolved in H_2O or MeOH before application. The reactant gas was isobutane. For chromatographic separations by HPLC and MPLC the following equipment was used: pump: Knauer HPLC Pump 64; detector: Knauer Differential Refractometer; integrator: Shimadzu C-R3A Chromatopac; fraction collector: Isco Cygnet Fraction Collector with a Knauer Peak Detector of the type 77; HPLC: precolumn: Nucleosil 100 C18 (30 mm×16 mm) (Knauer), separation column: Lichrosorb RP-18 (250×25 mm) (Merck); MPLC: separation column: column "Labochrom" containing Pyrex-borosilicate glass (750×10 mm) with adjustable adapters of Labomatic, length of the gel

Table 2
^{13}C NMR data[a] for 2,6-anhydroaldonic acids and derivatives, chemical shifts

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
1a[b]	173.2	78.7	68.7[d]	73.0	68.5[d]	69.7	—	—
1b [17][b]	171.7	78.7	68.7	72.9	68.3	69.8	—	53.2
1c[c]	167.8	76.0	67.3[d]	70.0	67.2[d]	66.2	—	52.5
1d[b]	174.5	79.3	68.8[d]	73.3	69.0[d]	70.1	—	—
2a[b]	173.0	78.4	70.2	73.9	66.3	68.6	—	—
2b[b]	171.2	78.2	70.1	73.7	66.2	68.8	—	53.0
2c[c]	167.0	76.1	68.6	71.0	65.8	66.7	—	52.5
2d[b]	174.3	78.6	69.7	74.0	66.4	69.0	—	—
3a[b]	174.1	74.3	69.2	70.0	66.6	64.7	—	—
3b[b]	172.7	74.5	69.2	70.1	66.5	64.8	—	53.2
3c[c]	168.3	73.3	67.5	67.5	66.0	63.6	—	52.7
3d[b]	175.1	74.3	69.1	70.3	66.5	64.5	—	—
4a[b]	173.2	78.7	71.5	77.1	68.9	68.8	—	—
4b[b]	171.6	78.8	71.5	77.0	69.1[d]	69.0[d]	—	53.2
4c[c]	167.7	76.3	69.2	71.8	68.3	66.1	—	52.8
4d[b]	174.1	79.1	71.7	77.3	69.2	69.0	—	—
4e[b]	69.1	69.7	77.8	70.0[d]	80.6[d]	61.2	—	—
5a[b]	174.4	74.0	69.2	70.9	66.6	75.2	61.3	—
5b[b]	173.0	74.3	69.3	70.9	66.6	75.4	61.3	53.2
5c[c]	168.0	73.4	67.4	67.8	66.0	72.3	62.3	52.7
5d[b]	175.4	74.0	69.3	70.9	66.5	75.0	61.2	—
6a[b]	173.9	74.1	71.0	70.1	64.1	75.7	61.7	—
6b[b]	172.4	75.8	71.0	70.0	64.1	74.3	61.7	53.0
6c[c]	167.2	73.5	69.0	66.0	64.8	72.1	62.7	52.2
6d[b]	175.2	74.5	70.4	70.0	64.2	75.8	61.8	—
7a [17][b]	173.2	78.6	68.6	73.9	69.0	79.1	61.4	—
7b [17,18][b]	171.8	78.8	68.6	73.8	69.0	79.3	61.4	53.2
7c[c]	167.4	76.8	66.6	71.4	67.1	74.6	61.5	52.8
7d [18][b]	174.6	78.7	69.1	73.9	69.1	78.9	61.5	—
7e [18] [18][b]	61.8[d]	80.3	67.6	74.3	69.5	78.7	61.7[d]	—
8a [19][b]	173.1	77.0	77.9	71.5	69.4	79.7	61.0	—
8b [19][b]	171.9	77.0	78.2	71.6	69.5	80.0	61.0	53.3
8c [19][c]	167.2	76.4	69.4	73.4	68.0	76.1	62.0	52.9
8d[b]	174.4	77.1	78.2	71.9	69.4	79.6	61.0	—
8e[b]	61.4	79.7	70.1	77.6	70.1	79.7	61.4	—
9a[b]	174.1	74.7	66.1	70.3	69.4	75.2	61.4	—
9b[b]	172.7	75.1	66.2	70.3	69.4	75.4	61.3	53.1
9c[c]	168.0	73.4	66.1	66.4	67.7	72.3	61.8	52.6
9d[b]	175.6	74.7	66.5	70.2	69.4	75.1	61.5	—
10a[b]	173.9	75.1	69.3[d]	68.5[d]	67.9	76.2	61.8	—
10b[b]	172.5	75.4	68.4[d]	69.4[d]	67.9	76.3	61.8	53.0
10c[c]	167.6	74.2	66.3[d]	65.6[d]	64.9	72.8	62.2	52.5
10d[b]	175.4	75.7	68.7	68.7	68.1	76.3	62.1	—
11a[b]	172.9	77.3	70.2	73.7	66.9	79.8	61.3	—
11b [19][b]	171.5	77.5	70.3	73.6	66.8	80.0	61.3	53.1
11c [19][c]	166.5	75.8	68.5	71.5	65.6	76.3	62.6	52.5
11d[b]	174.2	77.8	69.7	73.9	67.0	79.9	61.4	—
11e[b]	61.7[d]	78.7	69.5	74.3	67.6	80.3	61.8[d]	—
12a[b]	172.8	78.0	70.3	69.1	68.7	79.2	61.7	—
12b[b]	171.5	78.2	70.4	69.1	68.6	79.3	61.6	53.1
12c[c]	166.7	76.4	66.4	67.9	65.0	74.9	61.6	52.5
12d[b]	174.4	78.6	69.7	69.0	69.2	79.3	61.9	—
13a[b]	172.9	78.1	70.7	68.0	68.8	70.4	—	—
13b[b]	171.4	78.3	70.7	67.8	68.8	70.5	—	53.1
13c[c]	167.3	76.1	66.9	67.5	66.1	68.3	—	52.5
13d[b]	174.3	78.7	70.1	68.2	68.9	70.6	—	—

[a] Chemical shifts δ in ppm.
[b] Recorded in D_2O.
[c] Recorded in $CDCl_3$.
[d] Assignments may be interchanged.

Table 3
^{1}H NMR data[a] for 2,6-anhydroaldonic acids and derivatives, chemical shifts

Compound	H-2	H-3	H-4	H-5	H-6a	H-6b or H-7a	H-7b	OMe
1a[b]	3.702–3.746	3.702–3.746	3.583	3.882	3.846	3.576	—	—
1b [17][b]	3.790	3.732	3.582	3.882	3.842	3.574	—	3.681
1c[c]	3.998	5.376	5.119	5.287	4.106	3.695	—	3.742
1d[b]	3.591	3.654	3.560	3.875	3.577	3.860	—	—
2a[b]	4.102	4.188	3.511	3.683	3.074	3.853	—	—
2b[b]	4.202	4.174	3.520	3.707	3.103	3.906	—	3.670
2c[c]	4.218	5.720	5.070	5.238	3.298	4.281	—	3.723
2d[b]	3.947	4.110	3.505	3.718	3.118	3.942	—	—
3a[b]	4.014	3.676	4.018	3.722	3.459	3.667	—	—
3b[b]	4.053	3.662	4.015	3.717	3.447	3.659	—	3.676
3c[c]	4.222	5.123	5.587	5.014	3.674	3.948	—	3.718
3d[b]	3.862	3.608	4.034	3.714	3.433	3.656	—	—
4a[b]	3.766	3.410	3.350	3.514	3.203	3.891	—	—
4b[b]	3.827	3.407	3.346	3.512	3.205	3.891	—	3.681
4c[c]	3.976	5.127	5.205	4.964	3.374	4.218	—	3.722
4d[b]	3.648	3.378	3.336	3.515	3.189	3.895	—	—
5a[b]	4.051	3.616	4.060	3.506	3.544–3.594	3.755[d]	3.544–3.594[d]	—
5b[b]	4.094	3.612	4.051	3.501	3.532–3.582	3.748[d]	3.532–3.582[d]	3.685
5c[c]	4.306	5.144	5.668	4.957	3.996	4.186	4.186	3.730
5d[b]	3.938	3.579	4.051	3.515	3.565	3.586	3.752	—
6a[b]	4.400	4.051	3.930	3.678	3.606	3.606[d]	3.778[d]	—
6b[b]	4.444	4.043	3.921	3.602	3.670	3.774[d]	3.602[d]	3.674
6c[c]	4.432	5.128	5.287	4.969	3.922	4.110–4.163	4.110–4.163	3.623
6d[b]	4.230	4.004	3.932	3.674	3.584–3.644	3.584–3.644[d]	3.797[d]	—
7a [17][b]	3.770	3.680	3.554	3.853	3.595	3.660	3.596	—
7b [17][b]	3.813	3.675	3.547	3.851	3.593	3.648	3.589	3.692
7c[c]	3.971	5.346	5.079	5.427	3.919	4.145	4.145	3.735
7d[b]	3.628–3.684	3.628–3.684	3.550	3.848	3.581–3.617	3.628–3.684	3.581–3.617	—
8a[b]	3.386–3.446	3.845	3.386–3.446	3.302	3.350	3.598	3.767	—
8b[b]	3.377–3.434	3.887	3.377–3.434	3.291	3.346	3.585	3.760	3.692
8c [19,31][c]	3.990	5.181	5.238	5.078	3.696	4.232	4.133	3.727
8d[b]	3.360–3.423	3.725	3.360–3.423	3.315	3.343	3.612	3.762	—
9a[b]	4.079	3.861	3.927	3.729	3.794	3.635	3.586	—
9b[b]	4.114	3.852	3.919	3.725	3.778	3.623	3.579	3.688
9c[c]	4.274	5.238	5.343	4.945	4.109	4.067	4.142	3.723
9d[b]	3.958	3.813	3.915	3.727	3.809	3.636	3.591	—
10a[b]	4.425	3.923	3.931	3.581	3.806	3.738	3.631	—
10b[b]	4.468	3.905–3.930	3.905–3.930	3.582	3.802	3.738	3.627	3.687
10c[c]	4.453	5.079	5.079	4.803	4.083	4.200	4.243	3.727
10d[b]	4.235	3.926	3.872	3.580	3.814	3.746	3.647	—
11a[b]	4.232	4.187	3.595	3.469	3.279	3.619	3.797	—
11b[b]	4.283	4.179	3.591	3.464	3.272	3.619	3.795	3.681
11c [19,32][c]	4.265	5.667	5.053	5.201	3.648	4.230	4.139	3.678
11d[b]	4.050	4.126	3.584	3.466	3.310	3.622	3.817	—
12a[b]	4.192	4.139	3.723	3.789	3.534	3.759	3.634	—
12b[b]	4.233	4.125	3.712	3.788	3.518	3.748	3.627	3.691
12c [32][c]	4.286	5.548	5.095	5.247	3.901	4.201[d]	4.170[d]	3.687
12d[b]	3.994	4.078	3.708	3.786	3.554	3.764	3.649	—
13a[b]	4.118	4.123	3.740	3.819	3.954	3.560	—	—
13b[b]	4.182	4.121	3.738	3.820	3.956	3.563	—	3.684
13c[c]	4.237	5.558	5.124	5.103	4.235	3.712	—	3.717
13d[b]	3.913	4.050	3.720	3.817	3.984	3.567	—	—

[a] Chemical shifts δ in ppm.
[b] Recorded in D_2O.
[c] Recorded in $CDCl_3$.
[d] Assignments may be interchanged.

Table 4
^{1}H NMR data[a] for 2,6-anhydroaldonic acids and derivatives, coupling constants

Compound	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{4,5}$	$^3J_{5,6a}$	$^3J_{5,6b}/^3J_{6,7a}$	$^2J_{6a,6b}/^3J_{6,7b}$	$^2J_{7a,7b}$
1a	b	8.6	3.8	2.6	1.2	−12.6	—
1b [17]	9.1	8.9	3.4	2.7	1.3	−12.7	—
1c	8.1	8.9	3.3	4.0	2.0	−12.8	—
1d	9.5	9.5	~3.3	b	2.0	−13.6	—
2a	~1.0	3.2	9.6	b	b	b	—
2b	1.4	3.4	9.7	10.5	5.5	−11.2	—
2c	1.4	3.4	10.2	5.5	10.2	−11.3	—
2d	1.3	3.3	9.7	10.7	5.6	−11.1	—
3a	9.2	3.1	2.9	9.9	4.9	−11.1	—
3b	9.4	2.5	2.8	10.2	5.2	−11.0	—
3c	9.4	2.8	2.9	10.1	5.1	−11.1	—
3d	9.7	2.6	2.9	10.5	4.9	−10.8	—
4a	9.5	9.0	8.9	10.5	5.4	−11.3	—
4b	9.5	9.0	8.8	10.6	5.4	−11.3	—
4c	8.9	8.7	8.7	9.5	5.2	−11.6	—
4d	9.1	9.1	8.6	10.7	5.5	−11.2	—
5a	10.1	2.8	2.9	9.8	b	b	b
5b	10.1	2.6	2.8	10.0	b	b	b
5c	10.2	2.7	2.7	10.3	4.4	2.5	b
5d	10.1	2.7	2.6	9.9	5.4	~1.4	−14.5
6a	1.4	3.7	3.1	9.7	b	2.0	b
6b	1.5	3.7	3.1	8.6	~6.0	~5.5	−14.7
6c	1.5	3.7	3.1	10.4	~4.6	~3.4	b
6d	1.4	3.8	3.2	10.0	6.1	1.9	−11.7
7a [17]	9.6	9.5	3.3	1.2	9.0	3.2	−12.3
7b [17]	9.9	9.6	3.4	b	8.8	b	−12.4
7c	9.9	10.2	3.4	0.9	6.6	6.5	b
7d	b	8.5	3.3	< 0.5	8.8	3.8	−12.4
8a	b	b	b	9.7	5.6	2.1	−12.4
8b	b	b	b	9.6	5.7	2.0	−12.5
8c [19,31]	9.8	9.4	9.2	10.1	5.0	2.2	−12.5
8d	b	b	b	9.6	5.1	1.9	−12.4
9a	10.2	3.2	3.8	1.2	7.7	4.4	−12.0
9b	10.2	3.1	3.9	1.2	7.6	4.5	−11.8
9c	10.3	3.2	3.8	1.0	5.7	5.0	−9.3
9d	10.2	3.1	3.8	1.3	7.8	4.3	−11.9
10a	1.3	b	3.2	1.3	7.8	3.8	−11.7
10b	1.3	b	2.9	1.4	7.9	4.0	−11.8
10c	< 1.0	< 1.0	~3.1	1.4	6.8	6.0	−11.5
10d	1.2	3.2	2.9	1.2	8.1	3.5	−11.8
11a	1.2	3.4	9.7	9.7	6.4	1.9	−12.3
11b	1.2	3.5	9.6	9.8	6.4	2.1	−12.4
11c [19,32]	1.2	3.6	10.0	10.0	5.9	2.4	−12.4
11d	1.2	3.4	9.6	9.7	6.6	2.1	−12.3
12a	1.3	3.2	3.5	1.3	8.0	4.0	−11.9
12b	1.2	b	b	0.9	7.8	4.2	−11.9
12c [32]	1.5	3.9	3.7	1.3	6.4	6.4	−11.4
12d	1.3	~3.4	~3.3	~1.3	8.2	3.7	−12.0
13a	1.8	3.3	3.3	2.0	1.2	−12.8	—
13b	1.6	3.2	3.4	2.3	1.2	−12.8	—
13c	1.8	3.6	3.2	2.2	1.6	−13.3	—
13d	1.3	3.2	3.0	1.9	1.3	−12.7	—

[a] Coupling constants in Hz.
[b] Signals of higher order.

bed: 600 mm, filling: packed with cationic exchange resin of the type Dowex® 50 W X 4 (H^+-form), 200–400 mesh, and subsequently loaded with Nd^{3+}-solution ($NdCl_3 \times H_2O$, 15% solution) until a constant bed volume was reached.

General procedure (g.p.) 1: synthesis of methyl 2,6-anhydroaldonates from anhydrodeoxynitroalditols.—The anhydrodeoxynitroalditol (10 mmol) in H_2O (10 mL) was cooled on an ice bath and treated with H_2O_2 (30%, aq, 10 mL). K_2CO_3 (2.4 g)

Table 5
Observed CIMS ions for 2,6-anhydroaldonic acids and derivatives

Compounds	$[2M+H]^+$	$[M+H]^+$	$-ROH$	$-CO$	$-H_2O$	$-H_2O$	Other
1a–4a, 13a	357	179	161[a]	133	115	97	—
5a–12a	417	209/179[c]	191[a]/161[c]	163/133[c]	145/115[c]	127/97[c]	381[d]
1b–4b, 13b	385	193	161[b]	133	115	not found	175[e]
5b–12b	445	223	191[b]	163	145	127	391[f], 205[e]
Compounds	$[2M+H]^+$	$[M+H]^+$	$-HCO_2Me$	$-HOAc$	$-HOAc$	$-CH_2CO$	—
1c–4c, 13c	637	319	259/577[g]	199/517[g]	139/457[g]	97/415[g]	—
5c–12c	781	391	331/721[g]	271/661[g]	211/601[g]	169/559[g]	—
1d–4d, 13d	355	178	no further fragmentation observed				
5d–12d	415	208	no further fragmentation observed				

m/*z* for all values.
[a] R = H.
[b] R = Me.
[c] Fragmentation after loss of HCHO.
[d] $[2M+H-2H_2O]^+$.
[e] $[M+H-H_2O]^+$, no further fragmentation from this fragment observed.
[f] $[2M+H-3H_2O]^+$.
[g] Fragment of the dimer.

was added and the solution allowed to stand for 48 h at 20 °C. If the solution contained no peroxide after this time, further H_2O_2 (30%, aq, 5 mL) was added and the reaction time was extended for another 24 h. The excess of H_2O_2 was decomposed by addition of a small amount of MnO_2 (~1 mg) at 0 °C. After filtration, cation-exchange resin was added slowly until no further generation of CO_2 could be observed. The H_2O was distilled off at 30 °C and the crude anhydroaldonic acid dried under high vacuum overnight. The residue was dissolved in dry MeOH (100 mL) and heated for 16 h under reflux. During the last hour activated charcoal (~0.1 g) was added. After cooling, the solution was filtered and the HNO_3 removed by addition of anion-exchange resin. The ion exchanger was filtered off, and cation-exchange resin used to achieve neutrality. The methyl 2,6-anhydroaldonate was dried in vacuo.

General procedure (g.p.) 2: Acetylation of methyl 2,6-anhydroaldonates.—The methyl 2,6-anhydroaldonate (500 mg) in Ac_2O (1.5 mL) and abs. pyridine (2.2 mL) was stirred for 1 h at 0 °C, then allowed to warm to 20 °C. The progress of the reaction was monitored by TLC (*s.s.* 3). After complete conversion (6–16 h) the mixture was poured into ice–water (15 mL). After 2 h the solution was extracted with CH_2Cl_2, and the extract washed successively with HCl (5 M, aq), $NaHCO_3$ (satd, aq) and H_2O, dried ($NaSO_4$), and concentrated to a syrup. Residual traces of AcOH were removed by azeotropic distillation with toluene. The acetylated ester was crystallised in most cases from the solvent mentioned. Often prior purification by column chromatography was necessary.

General procedure (g.p.) 3: Synthesis of methyl 2,6-anhydroaldonates by deacetylation.—The fully *O*-acetylated methyl 2,6-anhydroaldonate (1 g) was kept for 1 h at 20 °C in dry MeOH (30 mL) containing NaOMe (1 M, 1 mL). The progress of the deacetylation was observed by TLC (*s.s.* 3). The solution was neutralised by addition of cation-exchange resin. The resin was filtered off and washed with MeOH. The combined eluates were concentrated to a syrup in vacuo.

General procedure (g.p.) 4: Synthesis of 2,6-anhydroaldonic acids from methyl 2,6-anhydroaldonates.—The methyl 2,6-anhydroaldonate (10 mmol) in NaOH (0.5 M, aq, 22 mL) was heated for 2 h at 60 °C. After cooling the Na^+-ions were removed by addition of cation-exchange resin. The resin was filtered off and washed with water. The solvent was removed by distillation at 35 °C.

General procedure (g.p.) 5: Synthesis of 2,6-anhydroaldonic acid amides from methyl 2,6-anhydroaldonates.—The methyl 2,6-anhydroaldonate (100 mg) in MeOH (5 mL), satd with NH_3 was kept for 6 h at ~5 °C. The solvent was removed by distillation and the amide was crystallised in most cases directly from H_2O or MeOH.

General procedure (g.p.) 6: Synthesis of anhydroalditols from methyl 2,6-anhydroaldonates.—An ice-cooled solution of the methyl 2,6-anhydroaldonate (2 mmol) in H_2O (20 mL) was

treated with cation-exchange resin (~5 mL volume). Freshly prepared $NaBH_4$ (0.3 M, aq, 25 mL) was added slowly under vigorous stirring at 0 °C. Subsequently solid $NaBH_4$ (~200 mg) was added and stirring continued for 1 h. The pH value was adjusted to 8–9 by addition of cation-exchange resin or solid sodium borohydride. The solution was kept for 12 h at ~5 °C and the Na^+-ions were removed by addition of cation-exchange resin. The resin was filtered off and washed with H_2O. The combined eluates were concentrated to dryness in vacuo. The solid was dissolved in MeOH and concentrated again to remove boric acid as trimethyl borate. This process was repeated until no trimethyl borate could be detected.

2,6-Anhydrohexonic acids.—Anal. Calcd for $C_6H_{10}O_6$ (178.14): C, 40.45; H, 5.66.

2,6-Anhydro-L-manno-*hexonic acid* (**1a**). Ester **1b** [17] (500 mg, 2.6 mmol) was saponified as described in g.p. 4 to give **1a** (460 mg, 99%): $[\alpha]_D$ +51.6°; R_f (*s.s.* 1) 0.29; CIMS: *m/z* (%) 357 (1), 179 (100), 161 (32), 133 (28), 115 (12), 97 (2). Anal. found: C, 40.30; H, 5.66.

2,6-Anhydro-D-galacto-*hexonic acid* (**2a**). Ester **2b** (400 mg, 2.08 mmol) was saponified as described in g.p. 4 to afford **2a** (326 mg, 88%): mp 152 °C (from H_2O); $[\alpha]_D$ −41.6°; R_f (*s.s.* 1) 0.30; IR (KBr): *ν* 3430 (O–H), 1720 (C=O), 1215, 1110, 1075 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 357 (1), 179 (100), 161 (38), 133 (72), 115 (14), 97 (7). Anal. found: C, 40.43; H, 5.68.

2,6-Anhydro-D-altro-*hexonic acid* (**13a**).—(a) 2,6-Anhydro-1-deoxy-1-nitro-D-*altro*-hexitol [13,15] (500 mg, 2.59 mmol) was converted as described in g.p. 1. The work-up was terminated before the esterification was started. **13a** crystallised directly after concentration of the mother liquor, containing HNO_3. Recrystallisation from H_2O afforded **13a** (275 mg, 60%): mp 228 °C (from H_2O); $[\alpha]_D$ −30.3°; R_f (*s.s.* 1) 0.19; IR (KBr): *ν* 3470 (O–H), 1690 (C=O), 1240, 1115, 980 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 357 (1), 179 (100), 161 (13), 133 (18), 115 (4), 97 (1). Anal. found: C, 40.38; H, 5.67.

2,6-Anhydro-D-altro-*hexonic acid* (**13a**). (b) Ester **13b** (150 mg, 0.78 mmol) was saponified as described in g.p. 4 to give **13a** (123 mg, 89%). The experimental data matched the values mentioned in procedure (a).

2,6-Anhydro-D-allo-*hexonic acid* (**3a**). Ester **3b** (400 mg, 2.08 mmol) was saponified as described in g.p. 4 to afford **3a** (324 mg, 88%): mp 84 °C (from H_2O); $[\alpha]_D$ −22.5°; R_f (*s.s.* 1) 0.34; IR (KBr): *ν* 3400 (O–H), 1720 (C=O), 1115, 1100, 1035 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 357 (2), 179 (100), 161 (21), 133 (27), 115 (11), 97 (5). Anal. found: C, 40.36; H, 5.68.

2,6-Anhydro-D-gulo-*hexonic acid* (**4a**). Ester **4b** [16] (384 mg, 2 mmol) was saponified as described in g.p. 4 to give **4a** (317 mg, 89%): mp 172 °C (from H_2O); $[\alpha]_D$ −9.2°; R_f (*s.s.* 1) 0.34; IR (KBr): *ν* 3360 (O–H), 1720 (C=O), 1095, 1055, 995 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 357 (2), 179 (100), 161 (12), 133 (18), 115 (26), 97 (12). Anal. found: C, 40.44; H, 5.65.

2,6-Anhydroheptonic acids.—Anal. Calcd for $C_7H_{12}O_7$ (208.17): C, 40.39; H, 5.81.

2,6-Anhydro-D-glycero-D-allo-*heptonic acid* (**5a**).—Ester **5b** (444 mg, 2 mmol) was saponified as described in g.p. 4 to afford **5a** (358 mg, 86%): mp 110 °C (from H_2O); $[\alpha]_D$ +13.4°; R_f (*s.s.* 1) 0.32; IR (KBr): *ν* 3530, 3400 (O–H), 1725 (C=O), 1210, 1195, 1085, 1045 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 417 (6), 381 (40), 209 (42), 191 (100), 163 (6), 145 (7), 127 (5), 179 (4), 161 (7), 133 (22), 115 (6), 97 (6). Anal. found: C, 40.30; H, 5.80.

2,6-Anhydro-D-glycero-D-gluco-*heptonic acid* (**6a**). Ester **6b** (444 mg, 2 mmol) was saponified as described in g.p. 4 to afford **6a** (342 mg, 82%): mp 155 °C (from H_2O); $[\alpha]_D$ +58.2°; R_f (*s.s.* 1) 0.24; IR (KBr): *ν* 3490, 3360 (O–H), 1720 (C=O), 1220, 1080, 1065 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 417 (1), 381 (1), 209 (32), 191 (100), 163 (32), 145 (27), 127 (7), 179 (76), 161 (3), 133 (5), 115 (7), 97 (3). Anal. found: C, 40.31; H, 5.83.

2,6-Anhydro-D-glycero-L-manno-*heptonic acid* (**7a**). Ester **7b** [3,17,18] (1.11 g, 5.00 mmol) was saponified as described in g.p. 4 to give **7a** (932 mg, 90%): mp 159 °C (from H_2O), lit. 177 °C [3,17]; $[\alpha]_D$ +53.8°, lit. $[\alpha]_{578}^{22}$ +62.5° (*c* 1.0, H_2O) [3], lit. $[\alpha]_D^{20}$ +57.8° (*c* 0.86, H_2O) [17]; R_f (*s.s.* 1) 0.19; IR (KBr): *ν* 3500, 3380, 3180 (O–H), 1700 (C=O), 1405 (O–H), 1100, 1075 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 417 (1), 381 (9), 209 (14), 191 (100), 163 (9), 145 (7), 127 (3), 179 (3), 161 (2), 133 (2), 115 (3), 97 (1). Anal. found: C, 40.26; H, 5.80.

2,6-Anhydro-D-glycero-D-gulo-*heptonic acid* (**8a**). Ester **8b** [3,19] (889 mg, 4 mmol) was saponified as described in g.p. 4 to give syrupy **8a** (830 mg, 100%): mp lit. 169 °C [3,19]; $[\alpha]_D$ +18.9°, lit. $[\alpha]_{578}^{22}$ +25.0° (*c* 1.0, H_2O) [3]; R_f (*s.s.* 1) 0.27; CIMS: *m/z* (%) 417 (2), 381 (1), 209 (36), 191 (100), 163 (18), 145 (13), 127 (11), 179 (82), 161 (38), 133 (14), 115 (36), 97 (4). Anal. found: C, 40.26; H, 5.79.

2,6-Anhydro-D-glycero-L-talo-*heptonic acid* (**9a**). Ester **9b** (400 mg, 1.8 mmol) was saponified as described in g.p. 4 to afford **9a** (369 mg, 98%): $[\alpha]_D$ −0.4°; R_f (*s.s.* 1) 0.29; CIMS: *m/z* (%) 417 (1), 381 (58), 209 (6), 191 (100), 163 (5), 145 (4), 127 (8), 179 (2), 161 (2), 133 (2), 115 (2), 97 (16). Anal. found: C, 40.38; H, 5.82.

2,6-Anhydro-D-glycero-L-ido-*heptonic acid* (**10a**). Ester **10b** (300 mg, 1.35 mmol) was saponified as described in g.p. 4 to give **10a** (277 mg, 99%): $[\alpha]_D$ +24.4°; R_f (*s.s.* 1) 0.27; CIMS: *m/z* (%) 417 (1), 381 (89), 209 (6), 191 (100), 163 (19), 145 (22), 127 (11), 179 (52), 161 (5), 133 (6), 115 (10), 97 (3). Anal. found: C, 40.25; H, 5.83.

2,6-Anhydro-D-glycero-D-galacto-*heptonic acid* (**11a**). Ester **11b** [19,20] (889 mg, 4 mmol) was saponified as described in g.p. 4 to afford **11a** (737 mg, 89%): mp 184 °C (from H_2O); $[\alpha]_D$ +1.7°; R_f (*s.s.* 1) 0.17; IR (KBr): ν 3380 (O–H), 1720 (C=O), 1235, 1160, 1110 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 417 (3), 381 (8), 209 (59), 191 (100), 163 (26), 145 (13), 127 (4), 179 (36), 161 (2), 133 (5), 115 (5), 97 (2). Anal. found: C, 40.28; H, 5.80.

2,6-Anhydro-D-glycero-L-altro-*heptonic acid* (**12a**). Ester **12b** (667 mg, 3 mmol) was saponified as described in g.p. 4 to give **12a** (548 mg, 88%): mp 169 °C (from H_2O); $[\alpha]_D$ +33.1°; R_f (*s.s.* 1) 0.15; IR (KBr): ν 3400 (O–H), 1750 (C=O), 1300 (O–H), 1250, 1225, 1140, 1120, 1100, 1035 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 417 (2), 381 (9), 209 (32), 191 (100), 163 (13), 145 (6), 127 (2), 179 (22), 161 (2), 133 (3), 115 (5), 97 (2). Anal. found: C, 40.36; H, 5.83.

Methyl 2,6-anhydrohexonates.—Anal. Calcd for $C_7H_{12}O_6$ (192.17): C, 43.75; H, 6.29.

Methyl 2,6-anhydro-L-manno-*hexonate* (**1b**). Ester **1c** (2 g, 6.28 mmol) was deacetylated as described in g.p. 3 to give **1b** (1.05 g, 87%): mp 100 °C (from EtOH–MeOH), lit. 92 °C [17]; $[\alpha]_D$ +42.2°, lit. $[\alpha]_D^{20}$ +21.1° (*c* 0.54, MeOH) [17]; R_f (*s.s.* 3) 0.57; IR (KBr): ν 3420 (O–H), 1730 (C=O), 1235, 1105 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 385 (9), 193 (100), 175 (2), 161 (2), 133 (5), 115 (3). Anal. found: C, 43.70; H, 6.31.

Methyl 2,6-anhydro-D-galacto-*hexonate* (**2b**). 2,6-Anhydro-1-deoxy-1-nitro-D-*galacto*-hexitol [6,15,33] (1.5 g, 7.77 mmol) was converted as described in g.p. 1 to give **2b** (1.14 g, 76%): mp 171 °C (from MeOH); $[\alpha]_D$ −30.4°; R_f (*s.s.* 3) 0.51; IR (KBr): ν 3380 (O–H), 1740 (C=O), 1260 (O–H), 1105, 1075 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 385 (7), 193 (100), 175 (8), 161 (1), 133 (2), 115 (4). Anal. found: C, 43.76; H, 6.30.

Methyl 2,6-anhydro-D-altro-*hexonate* (**13b**). (a) One drop of conc. H_2SO_4 was added to a solution of **13a** (178 mg, 1 mmol) in dry MeOH (5 mL) and heated for 12 h under reflux. After cooling to 20 °C the solution was neutralised with Amberlite IRA-400 (HCO_3^-). The resin was filtered off, washed successively with H_2O and the combined solutions were concentrated to afford **13b** (158 mg, 82%): mp 105 °C (from MeOH); $[\alpha]_D$ −31.5°; R_f (*s.s.* 3) 0.67; IR (KBr): ν 3400 (O–H), 1725 (C=O), 1225, 1100 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 385 (93), 193 (100), 175 (2), 161 (4), 133 (8), 115 (2). Anal. found: C, 43.75; H, 6.31.

Methyl 2,6-anhydro-D-altro-*hexonate* (**13b**). (b) A mixture of 2,6-anhydro-1-deoxy-1-nitro-D-*altro*-hexitol [13,15] and 2,6-anhydro-1-deoxy-1-nitro-D-*allo*-hexitol [13,15] (1 g, 5.18 mmol) was converted as described in g.p. 1. The syrup (915 mg), containing crude methyl 2,6-anhydro-D-*altro*-hexonate (**13b**) and methyl 2,6-anhydro-D-*allo*-hexonate (**3b**), was separated by MPLC with H_2O as eluent at a flow of 0.5 mL/min. The second fraction contained **13b** (379 mg, 38%). The experimental data matched the values mentioned in procedure (a).

Methyl 2,6-anhydro-D-allo-*hexonate* (**3b**). (a) 2,6-Anhydro-1-deoxy-1-nitro-D-*allo*-hexitol [13,15] (579 mg, 3 mmol) was converted as described in g.p. 1. The crude ester was purified by MPLC with H_2O as eluent at a flow of 0.5 mL/min to give **3b** (407 mg, 71%): mp 82 °C (from H_2O); $[\alpha]_D$ −29.9°; R_f (*s.s.* 3) 0.67; IR (KBr): ν 3390 (O–H), 1725 (C=O), 1095, 1035 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 385 (87), 193 (100), 175 (11), 161 (9), 133 (5), 115 (2). Anal. found: C, 43.62; H, 6.28.

Methyl 2,6-anhydro-D-allo-*hexonate* (**3b**). (b) A mixture of 2,6-anhydro-1-deoxy-1-nitro-D-*allo*-hexitol [13,15] and 2,6-anhydro-1-deoxy-1-nitro-D-*altro*-hexitol [13,15] (1 g, 5.18 mmol) was converted as described for **13b**. The first MPLC-fraction contained **3b** (335 mg, 34%). The experimental data matched the values mentioned in procedure (a).

Methyl 2,6-anhydro-D-gulo-*hexonate* (**4b**). Ester **4c** (3 g, 9.43 mmol) was deacetylated as described in g.p. 3 to afford **4b** (1.65 g, 91%): mp 101 °C (from MeOH); $[\alpha]_D$ −25.8°; R_f (*s.s.* 3) 0.64; IR (KBr): ν 3380 (O–H), 1730 (C=O), 1220, 1090, 1055 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 385 (99), 193 (100), 175 (8), 161 (1), 133 (3), 115 (5). Anal. found: C, 43.68; H, 6.29.

Methyl 2,6-anhydroheptonates.—Anal. Calcd for $C_8H_{14}O_7$ (222.20): C, 43.24; H, 6.35.

Methyl 2,6-anhydro-D-glycero-D-allo-*heptonate* (**5b**). 2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-D-*allo*-heptitol [15,19] (446 mg, 2 mmol) was converted as described in g.p. 1. The crude ester (400 mg) was purified by HPLC at a flow of 2 mL/min with H_2O as eluent to give **5b** (322 mg, 73%): mp 85 °C (from MeOH); $[\alpha]_D$ +13.5°; R_f (*s.s.* 3) 0.51; IR (KBr): ν 3480, 3420 (O–H), 1675 (C=O), 1245, 1125, 1115, 1080, 945 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (19), 391 (14), 223 (100), 205 (3), 191 (85), 163 (3), 145 (5), 127 (3). Anal. found: C, 43.11; H, 6.37.

Methyl 2,6-anhydro-D-glycero-D-gluco-*heptonate* (**6b**). Ester **6c** (1 g, 2.56 mmol) was deacetylated as described in g.p. 3 to afford **6b** (520 mg, 91%): mp 141 °C (from H_2O); $[\alpha]_D$ +63.8°; R_f (*s.s.* 3) 0.49; IR (KBr): ν 3450, 3330 (O–H), 1725 (C=O), 1220, 1145, 1070 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (92), 391 (27), 223 (100), 205 (10), 191 (5), 163 (3), 145 (4), 127 (3). Anal. found: C, 43.27; H, 6.37.

Methyl 2,6-anhydro-D-glycero-L-manno-*heptonate* (**7b**). Ester **7c** (3 g, 7.69 mmol) was deacetylated as described in g.p. 3 to give **7b** (1.53 g, 90%): mp 109 °C (from MeOH), lit. 141 °C [3,17], lit. 121–123 °C [18]; $[\alpha]_D$ +48.4°, lit. $[\alpha]_{578}^{22}$ +56.5° (*c* 1.0, H_2O) [3], lit. $[\alpha]_D^{20}$ +57.5° (*c* 1.11, H_2O) [17], lit. $[\alpha]_D^{20}$ −32° (*c* 0.12, H_2O) [18]; R_f (*s.s.* 3) 0.44; IR (KBr): ν 3360 (O–H), 1730 (C=O), 1245, 1085 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (82), 391 (7), 223 (100), 205 (78), 191 (12), 163 (3), 145 (2), 127 (2). Anal. found: C, 43.22; H, 6.33.

Methyl 2,6-anhydro-D-glycero-D-gulo-*heptonate* (**8b**). Ester **8c** [1,19,26,31] (3 g, 7.69 mmol) was deacetylated as described in g.p. 3 to give **8b** (1.49 g, 87%): mp 121 °C (from H_2O–EtOH), lit. 119 °C [3], lit. 116 °C [19]; $[\alpha]_D$ +14.7°, lit. $[\alpha]_{578}^{22}$ +16.5° (*c* 1.0, H_2O) [3]; R_f (*s.s.* 3) 0.60; IR (KBr): ν 3400 (O–H), 1730 (C=O), 1100, 1075 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (88), 391 (13), 223 (100), 205 (8), 191 (14), 163 (3), 145 (4), 127 (4). Anal. found: C, 43.18; H, 6.34.

Methyl 2,6-anhydro-D-glycero-L-talo-*heptonate* (**9b**). Ester **9c** (1 g, 2.56 mmol) was deacetylated as described in g.p. 3 to afford **9b** (563 mg, 99%): $[\alpha]_D$ −5.3°; R_f (*s.s.* 3) 0.57; CIMS: *m/z* (%) 445 (97), 391 (7), 223 (100), 205 (60), 191 (57), 163 (5), 145 (4), 127 (3). Anal. found: C, 43.15; H, 6.36.

Methyl 2,6-anhydro-D-glycero-L-ido-*heptonate* (**10b**). 2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-L-*ido*-heptitol [34] (2.23 g, 10 mmol) was converted as described in g.p. 1. The crude ester (1.9 g) was purified in several runs by HPLC at a flow of 4 mL/min with H_2O as eluent to give **10b** (1.83 g, 82%): $[\alpha]_D$ +34.3°; R_f (*s.s.* 3) 0.60; CIMS: *m/z* (%) 445 (12), 391 (14), 223 (100), 205 (11), 191 (26), 163 (4), 145 (3), 127 (1). Anal. found: C, 43.33; H, 6.36.

Methyl 2,6-anhydro-D-glycero-D-galacto-*heptonate* (**11b**). 2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-D-*galacto*-heptitol [6,15,19,27,33] (4.46 g, 20 mmol) was converted as described in g.p. 1 to afford **11b** (3.82 g, 86%): mp 158 °C (from MeOH), lit. 99 °C [19]; $[\alpha]_D$ +5.1°; R_f (*s.s.* 3) 0.36; IR (KBr): ν 3470, 3380 (O–H), 1710 (C=O), 1095, 1065 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (81), 391 (22), 223 (100), 205 (13), 191 (7), 163 (3), 145 (3), 127 (2). Anal. found: C, 43.28; H, 6.37.

Methyl 2,6-anhydro-D-glycero-L-altro-*heptonate* (**12b**). 2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-L-*altro*-heptitol [34] (446 mg, 2 mmol) was converted as described in g.p. 1. The crude ester (420 mg) was purified by MPLC with H_2O as eluent at a flow of 0.5 mL/min to give **12b** (340 mg, 77%): mp 162 °C (from H_2O–MeOH); $[\alpha]_D$ +35.5°; R_f (*s.s.* 3) 0.34; IR (KBr): ν 3400 (O–H), 1750 (C=O), 1250, 1145, 1120, 1095, 1035 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 445 (95), 391 (12), 223 (100), 205 (53), 191 (14), 163 (2), 145 (3), 127 (1). Anal. found: C, 43.34; H, 6.36.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydrohexonates*.—Anal. Calcd for $C_{13}H_{18}O_9$ (318.28): C, 49.06; H, 5.70.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydro*-L-manno-*hexonate* (**1c**). 2,6-Anhydro-1-deoxy-1-nitro-L-*manno*-hexitol [6,15,17,33] (1.93 g, 10 mmol) was converted as described in g.p. 1. The unprotected ester **1b** [17] (1.78 g) was acetylated as described in g.p. 2. Column chromatography on silica gel with *s.s.* 4 afforded **1c** (2.26 g, 71%): mp 76 °C (from Et_2O); $[\alpha]_D$ +18.2°; R_f (*s.s.* 4) 0.48; ^{1}H NMR ($CDCl_3$): δ 1.995, 2.039, 2.100 (3s, 9 H, 3×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.6, 20.6, 20.8, 169.6, 169.7, 170.2 (3×Ac), *cf.* Table 2; IR (KBr): ν 1750 (C=O), 1230, 1055 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 637 (2), 577 (1), 517 (1), 457 (1), 415 (1), 319 (57), 259 (100), 199 (18), 139 (8), 97 (1). Anal. found: C, 48.87; H, 5.68.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydro*-D-galacto-*hexonate* (**2c**). Ester **2b** (192 mg, 1 mmol) was acetylated as described in g.p. 2 to give **2c** (280 mg, 88%): mp 139 °C (from EtOAc–Et_2O); $[\alpha]_D$ −84.3°; R_f (*s.s.* 4) 0.31; ^{1}H NMR ($CDCl_3$): δ 1.983, 2.010, 2.075 (3s, 9 H, 3×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.6, 169.6, 169.6, 169.9

(3×Ac), *cf*. Table 2; IR (KBr): ν 1755 (C=O), 1250, 1210, 1060 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 637 (5), 577 (1), 517 (1), 457 (1), 415 (1), 319 (100), 259 (79), 199 (12), 139 (5), 97 (1). Anal. found: C, 48.96; H, 5.70.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydro*-D-altro-*hexonate* (**13c**). Ester **13b** (192 mg, 1 mmol) was acetylated as described in g.p. 2 and then purified by column chromatography on silica gel with *s.s.* 5 giving **13c** (265 mg, 83%): $[\alpha]_D$ +17.5°; R_f (*s.s.* 5) 0.44; ^{1}H NMR ($CDCl_3$): δ 1.959, 2.037, 2.072 (3s, 9 H, 3×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.4, 20.9, 169.5, 169.7, 170.3 (3×Ac), *cf*. Table 2; IR (CCl_4): ν 1730 (C=O), 1250, 1215 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 637 (63), 577 (8), 517 (2), 457 (1), 415 (35), 319 (100), 259 (82), 199 (11), 139 (9), 97 (50). Anal. found: C, 49.10; H, 5.69.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydro*-D-allo-*hexonate* (**3c**). Ester **3b** (192 mg, 1 mmol) was acetylated as described in g.p. 2. Column chromatography on silica gel with *s.s.* 4 afforded **3c** (278 mg, 87%): $[\alpha]_D$ −14.9°; R_f (*s.s.* 4) 0.48; ^{1}H NMR ($CDCl_3$): δ 1.979, 1.981, 2.124 (3s, 9 H, 3×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.6, 169.1, 169.3, 169.7 (3×Ac), *cf*. Table 2; IR (CCl_4): ν 1750 (C=O), 1220, 1050 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 637 (7), 577 (1), 517 (1), 457 (1), 415 (1), 319 (100), 259 (12), 199 (2), 139 (4), 97 (1). Anal. found: C, 49.05; H, 5.72.

Methyl 3,4,5-tri-O-*acetyl-2,6-anhydro*-D-gulo-*hexonate* (**4c**). 1,5-Anhydro-6-deoxy-6-nitro-L-*gluco*-hexitol [15,22] (1.93 g, 10 mmol) was converted as described in g.p. 1. The unprotected ester **4b** [16] (1.85 g) was acetylated as described in g.p. 2. Column chromatography on silica gel with *s.s.* 5 gave **4c** (2.24 g, 70%): mp 113 °C (from EtOAc–Et_2O); $[\alpha]_D$ −40.1°; R_f (*s.s.* 5) 0.72; ^{1}H NMR ($CDCl_3$): δ 2.008, 2.012, 2.013 (3s, 9 H, 3 ×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.6, 169.5, 169.6, 169.9 (3×Ac), *cf*. Table 2; IR (KBr): ν 1750 (C=O), 1230, 1055 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 637 (21), 577 (16), 517 (4), 457 (2), 415 (3), 319 (81), 259 (100), 199 (20), 139 (13), 97 (2). Anal. found: C, 48.92; H, 5.70.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydrohept-onates*.—Anal. Calcd for $C_{16}H_{22}O_{11}$ (390.34): C, 49.23; H, 5.68.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-D-allo-*heptonate* (**5c**). Ester **5b** (667 mg, 3 mmol) was acetylated as described in g.p. 2 and purified by column chromatography on silica gel with *s.s.* 5 to give **5c** (911 mg, 78%): mp 75 °C (from MeOH–Et_2O); $[\alpha]_D$ +6.3°; R_f (*s.s.* 5) 0.67; ^{1}H NMR ($CDCl_3$): δ 1.978, 2.049, 2.139, 2.150 (4s, 12 H, 4×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.7, 20.8, 168.9, 169.0, 169.7, 170.7 (4×Ac), *cf*. Table 2; IR (KBr): ν 1750 (C=O), 1230, 1050 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 781 (19), 721 (67), 661 (84), 601 (22), 559 (18), 391 (100), 331 (31), 271 (18), 211 (8), 169 (2). Anal. found: C, 49.06; H, 5.66.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-D-gluco-*heptonate* (**6c**). 2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-D-*gluco*-heptitol [34] (1.34 g, 6 mmol) was converted as described in g.p. 1. The unprotected crude ester **6b** (1.22 g) was first acetylated as described in g.p. 2 and then purified by column chromatography on silica gel with *s.s.* 4. The eluate crystallised in needles after concentration of the column fraction giving **6c** (1.65 g, 71%): mp 119 °C; $[\alpha]_D$ −10.3°; R_f (*s.s.* 4) 0.27; ^{1}H NMR ($CDCl_3$): δ 1.868, 1.962, 1.995, 2.042 (4s, 12 H, 4×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.2, 20.3, 20.4, 20.5, 168.6, 168.8, 169.0, 170.4 (4×Ac), *cf*. Table 2; IR (KBr): ν 1740 (C=O), 1250, 1225, 1150, 1050 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 781 (20), 721 (23), 661 (4), 601 (2), 559 (3), 391 (100), 331 (41), 271 (5), 211 (9), 169 (2). Anal. found: C, 49.05; H, 5.67.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-L-manno-*heptonate* (**7c**).—2,6-Anhydro-7-deoxy-7-nitro-L-*glycero*-L-*galacto*-heptitol [15,17,35,36] (4.46 g, 20 mmol) was converted as described in g.p. 1. The unprotected ester **7b** [3,17,18] (4.12 g) was acetylated as described in g.p. 2. **7c** (4.13 g) crystallised directly from Et_2O. Column chromatography on silica gel with *s.s.* 7 and crystallisation from Et_2O afforded another 1.62 g of **7c** (5.75 g, 74%): mp 150 °C; $[\alpha]_D$ +17.4°; R_f (*s.s.* 7) 0.50; ^{1}H NMR ($CDCl_3$): δ 1.971, 2.017, 2.023, 2.144 (4s, 12 H, 4×Ac), *cf*. Table 3; ^{13}C NMR ($CDCl_3$): δ 20.6, 20.6, 20.6, 20.6, 169.6, 170.0, 170.2, 170.4 (4×Ac), *cf*. Table 2; IR (KBr): ν 1740 (C=O), 1265, 1230 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 781 (5), 721 (7), 661 (2), 601 (1), 559 (4), 391 (100), 331 (87), 271 (18), 211 (14), 169 (8). Anal. found: C, 49.11; H, 5.66.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-D-gulo-*heptonate* (**8c**).—2,6-Anhydro-1-deoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol [15,19,36,37] (4.46 g, 20 mmol) was converted as described in g.p. 1. The unprotected ester **8b** [3,19] (4.23 g) was acetylated as described in g.p. 2. Column chromatography on silica gel with *s.s.* 7 afforded **8c** (5.84 g,

75%): mp 152 °C (from EtOAc–Et_2O), lit. 107–109 °C [1], lit. 142 °C [19], lit. 145–146 °C [26], lit. 149 °C [31]; $[\alpha]_D$ +3.7°, lit. $[\alpha]_D^{20}$ +20.18° (*c* ~4, $CHCl_3$) [1], lit. $[\alpha]_D^{20}$ +5° (*c* 5, $CHCl_3$) [26], lit. $[\alpha]_{589}^{23}$ −23° (*c* 0.2, $CHCl_3$) [31]; R_f (*s.s.* 7) 0.52; ^1H NMR ($CDCl_3$): δ 1.993, 2.001, 2.006, 2.065 (4s, 12 H, 4×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.6, 20.7, 169.3, 169.3, 170.2, 170.6 (4×Ac), *cf.* Table 2; IR (KBr): ν 1740 (C=O), 1250, 1220 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 781 (11), 721 (7), 661 (2), 601 (1), 559 (2), 391 (100), 331 (72), 271 (9), 211 (10), 169 (7). Anal. found: C, 49.08; H, 5.67.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-L-talo-*heptonate* (**9c**).—2,6-Anhydro-7-deoxy-7-nitro-L-*glycero*-L-*gluco*-heptitol [34] (2.23 g, 10 mmol) was converted as described in g.p. 1. The unprotected ester **9b** (2.05 g) was acetylated as described in g.p. 2. Column chromatography on silica gel with *s.s.* 4 afforded **9c** (3.05 g, 78%): $[\alpha]_D$ +8.8°; R_f (*s.s.* 4) 0.42; ^1H NMR ($CDCl_3$): δ 1.949, 2.001, 2.118, 2.121 (4s, 12 H, 4×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.7, 20.7, 20.7, 168.8, 169.1, 169.4, 170.4 (4×Ac), *cf.* Table 2; IR (CCl_4): ν 1745 (C=O), 1260, 1225, 1055 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 781 (19), 721 (6), 661 (7), 601 (3), 559 (2), 391 (100), 331 (69), 271 (16), 211 (13), 169 (3). Anal. found: C, 49.08; H, 5.66.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-L-ido-*heptonate* (**10c**).—Ester **10b** (300 mg, 1.35 mmol) was acetylated as described in g.p. 2 and purified by column chromatography on silica gel with *s.s.* 6 to afford **10c** (412 mg, 79%): mp 119 °C (from Et_2O); $[\alpha]_D$ −13.1°; R_f (*s.s.* 6) 0.69; ^1H NMR ($CDCl_3$): δ 2.024, 2.031, 2.067, 2.127 (4s, 12 H, 4×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.5, 20.6, 20.7, 20.7, 167.9, 169.1, 169.4, 170.5 (4×Ac), *cf.* Table 2; IR (KBr): ν 1740 (C=O), 1240, 1210, 1050 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 781 (8), 721 (6), 661 (2), 601 (1), 559 (1), 391 (100), 331 (95), 271 (22), 211 (15), 169 (17). Anal. found: C, 49.11; H, 5.68.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-D-galacto-*heptonate* (**11c**).—Ester **11b** [19,20] (300 mg, 1.35 mmol) was acetylated as described in g.p. 2. **11c** (290 mg) crystallised directly from 1:1 EtOAc–Et_2O. The remaining syrup was purified by column chromatography on silica gel with *s.s.* 2 and crystallised from 1:1 EtOAc–Et_2O to give another 166 mg of **11c** (456 mg, 87%): mp 102 °C, lit. 93 °C [19]; $[\alpha]_D$ −42.2°, lit. $[\alpha]_D^{25}$ −44.0° (*c* not indicated, $CHCl_3$) [32]; R_f (*s.s.* 2) 0.54; ^1H NMR ($CDCl_3$): δ 1.920, 1.979, 2.020, 2.047 (4s, 12 H, 4×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.4, 20.5, 20.6, 169.4, 169.6, 169.8, 170.5 (4×Ac), *cf.* Table 2; IR (KBr): ν 1745 (C=O), 1230, 1060 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 781 (16), 721 (4), 661 (1), 601 (1), 559 (2), 391 (100), 331 (68), 271 (9), 211 (9), 169 (7). Anal. found: C, 49.04; H, 5.68.

Methyl 3,4,5,7-tetra-O-*acetyl-2,6-anhydro*-D-glycero-L-altro-*heptonate* (**12c**).—Ester **12b** (222 mg, 1 mmol) was acetylated as described in g.p. 2 and purified by column chromatography on silica gel with *s.s.* 7 to afford **12c** (333 mg, 85%): mp 119 °C (from EtOAc); $[\alpha]_D$ +35.5°, lit. $[\alpha]_D^{25}$ −24.0° (*c* not indicated, $CHCl_3$) [32]; R_f (*s.s.* 7) 0.47; ^1H NMR ($CDCl_3$): δ 1.910, 1.973, 2.005, 2.045 (4s, 12 H, 4×Ac), *cf.* Table 3; ^{13}C NMR ($CDCl_3$): ° 20.3, 20.4, 20.4, 20.5, 169.3, 169.5, 170.0, 170.3 (4×Ac), *cf.* Table 2; IR (KBr): ν 1730 (C=O), 1220, 1060 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 781 (3), 721 (1), 661 (1), 601 (1), 559 (1), 391 (100), 331 (29), 271 (4), 211 (6), 169 (4). Anal. found: C, 49.23; H, 5.68.

2,6-Anhydrohexonamides.—Anal. Calcd for $C_6H_{11}NO_5$ (177.16): C, 40.68; H, 6.26; N, 7.91.

2,6-Anhydro-L-manno-*hexonamide* (**1d**). Ester **1b** [17] (100 mg, 0.52 mmol) was converted as described in g.p. 5 giving **1d** (90 mg, 98%): $[\alpha]_D$ −70.7°; R_f (*s.s.* 3) 0.24; CIMS: *m/z* (%) 355 (6), 178 (100). Anal. found: C, 40.52; H, 6.24; N, 7.93.

2,6-Anhydro-D-galacto-*hexonamide* (**2d**). Ester **2b** (200 mg, 1.04 mmol) was converted as described in g.p. 5 to afford **2d** (172 mg, 93%): mp 177 °C (from aq MeOH); $[\alpha]_D$ −4.4°; R_f (*s.s.* 3) 0.32; IR (KBr): ν 3400, 3360, 3300, 3200 (O–H, N–H), 1670 (C=O), 1105, 1080 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 355 (94), 178 (100). Anal. found: C, 40.60; H, 6.25; N, 7.89.

2,6-Anhydro-D-altro-*hexonamide* (**13d**). Ester **13b** (100 mg, 0.52 mmol) was converted as described in g.p. 5 giving **13d** (92 mg, 100%): $[\alpha]_D$ −65.2°; R_f (*s.s.* 3) 0.41; CIMS: *m/z* (%) 355 (69), 178 (100). Anal. found: C, 40.80; H, 6.26; N, 7.94.

2,6-Anhydro-D-allo-*hexonamide* (**3d**). Ester **3b** (100 mg, 0.52 mmol) was converted as described in g.p. 5 affording **3d** (90 mg, 98%): $[\alpha]_D$ −13.8°; R_f (*s.s.* 3) 0.36; CIMS: *m/z* (%) 355 (70), 178 (100). Anal. found: C, 40.60; H, 6.24; N, 7.93.

2,6-Anhydro-D-gulo-*hexonamide* (**4d**). Ester **4b** [16] (200 mg, 1.04 mmol) was converted as described in g.p. 5 to afford **4d** (175 mg, 95%): mp 172 °C (from H_2O–MeOH); $[\alpha]_D$ −11.9°; R_f (*s.s.* 3) 0.36;

IR (KBr): ν 3390 (O–H, N–H), 1620 (C=O), 1110, 1080 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 355 (32), 178 (100). Anal. found: C, 40.58; H, 6.27; N, 7.90.

2,6-Anhydroheptonamides.—Anal. Calcd for $C_7H_{13}NO_6$ (207.18): C, 40.58; H, 6.32; N, 6.76.

2,6-Anhydro-D-glycero-D-allo-*heptonamide* (**5d**). Ester **5b** (100 mg, 0.45 mmol) was converted as described in g.p. 5 to afford **5d** (81 mg, 87%): mp 182 °C (from H_2O); $[\alpha]_D$ +21.0°; R_f (*s.s.* 3) 0.30; IR (KBr): ν 3380, 3200 (O–H, N–H), 1675 (C=O), 1065, 1035 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (12), 208 (100). Anal. found: C, 40.44; H, 6.33; N, 6.73.

2,6-Anhydro-D-glycero-D-gluco-*heptonamide* (**6d**). Ester **6b** (200 mg, 0.9 mmol) was converted as described in g.p. 5 to give **6d** (173 mg, 93%): mp 183 °C (from H_2O); $[\alpha]_D$ +154.6°; R_f (*s.s.* 3) 0.27; IR (KBr): ν 3300 (O–H, N–H), 1660 (C=O), 1125, 1110, 1070 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (6), 208 (100). Anal. found: C, 40.47; H, 6.32; N, 6.76.

2,6-Anhydro-D-glycero-L-manno-*heptonamide* (**7d**). Ester **7b** [3,17,18] (200 mg, 0.9 mmol) was converted as described in g.p. 5 to afford **7d** (172 mg, 92 %): mp 194 °C (from H_2O), lit. 196–197 °C [18]; $[\alpha]_D$ +59.1°, lit. $[\alpha]_D^{20}$ +67.8° (*c* 1.15, H_2O) [18]; R_f (*s.s.* 3) 0.21; IR (KBr): ν 3390, 3310 (O–H, N–H), 1655 (C=O), 1105, 1075, 1055 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (15), 208 (100). Anal. found: C, 40.49; H, 6.32; N, 6.75.

2,6-Anhydro-D-glycero-D-gulo-*heptonamide* (**8d**). Ester **8b** [3,19] (200 mg, 0.9 mmol) was converted as described in g.p. 5 to afford **8d** (160 mg, 86%): mp 205 °C (from H_2O–MeOH); $[\alpha]_D$ +29.0°; R_f (*s.s.* 3) 0.27; IR (KBr): ν 3400, 3260, 3140 (O–H, N–H), 1655 (C=O), 1080, 1055 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (10), 208 (100). Anal. found: C, 40.51; H, 6.30; N, 6.77.

2,6-Anhydro-D-glycero-L-talo-*heptonamide* (**9d**). Ester **9b** (100 mg, 0.45 mmol) was converted as described in g.p. 5 giving **9d** (88 mg, 96%): $[\alpha]_D$ +1.5°; R_f (*s.s.* 3) 0.24; CIMS: *m/z* (%) 415 (12), 208 (100). Anal. found: C, 40.58; H, 6.33; N, 6.76.

2,6-Anhydro-D-glycero-L-ido-*heptonamide* (**10d**). Ester **10b** (200 mg, 0.9 mmol) was converted as described in g.p. 5 affording **10d** (185 mg, 99%): $[\alpha]_D$ +72.7°; R_f (*s.s.* 3) 0.43; CIMS: *m/z* (%) 415 (20), 208 (100). Anal. found: C, 40.66; H, 6.35; N, 6.79.

2,6-Anhydro-D-glycero-D-galacto-*heptonamide* (**11d**). Ester **11b** [19,20] (200 mg, 0.9 mmol) was converted as described in g.p. 5 to afford **11d** (169 mg, 91%): mp 218 °C (from H_2O); $[\alpha]_D$ +39.4°; R_f (*s.s.* 3) 0.18; IR (KBr): ν 3390, 3320, 3230 (O–H, N–H), 1670 (C=O), 1105, 1065 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (18), 208 (100). Anal. found: C, 40.54; H, 6.34; N, 6.73.

2,6-Anhydro-D-glycero-L-altro-*heptonamide* (**12d**). Ester **12b** (200 mg, 0.9 mmol) was converted as described in g.p. 5 to afford **12d** (172 mg, 92%): mp 210 °C (from H_2O); $[\alpha]_D$ +74.7°; R_f (*s.s.* 3) 0.14; IR (KBr): ν 3430, 3330, 3250 (O–H, N–H), 1675 (C=O), 1105, 1070 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 415 (14), 208 (100). Anal. found: C, 40.52; H, 6.30; N, 6.75.

Anhydrohexitol.—Anal. Calcd for $C_6H_{12}O_5$ (164.16): C, 43.90; H, 7.37.

1,5-Anhydro-L-gluco-*hexitol* (**4e**). Ester **4b** [16] (500 mg, 2.6 mmol) was converted as described in g.p. 6 to afford **4e** (385 mg, 90%): mp 140 °C (from MeOH), lit. 141–142 °C [22]; $[\alpha]_D$ −40.6°, lit. $[\alpha]_D^{25}$ −40.4° (*c* 2.6, H_2O) [22]; R_f (*s.s.* 3) 0.36; ^{1}H NMR (D_2O): δ 3.134 (dd, 1 H, $J_{1a,1b}$ −11.2 Hz, $J_{1a,2}$ 10.8 Hz, H-1a), 3.182–3.234 (dd, 1 H, $J_{4,5}$ ABX, H-4), 3.182–3.234 (ddd, 1 H, $J_{5,6a}$ 5.6 Hz, $J_{5,6b}$ 1.9 Hz, H-5), 3.292 (dd, 1 H, $J_{3,4}$ 8.9 Hz, H-3), 3.448 (ddd, 1 H, $J_{2,3}$ 9.1 Hz, H-2), 3.541 (dd, 1 H, $J_{6a,6b}$ −12.1 Hz, H-6a), 3.738 (dd, 1 H, H-6b), 3.840 (dd, 1 H, $J_{1b,2}$ 5.4 Hz, H-1b); IR (KBr): ν 3410, 3340, 3240 (O–H), 1105, 1075, 1010 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 329 (88), 311 (1), 293 (2), 165 (100), 147 (4), 129 (46). Anal. found: C, 43.73; H, 7.37.

Anhydroheptitols.—Anal. Calcd for $C_7H_{14}O_6$ (194.19): C, 43.30; H, 7.27.

2,6-Anhydro-L-glycero-L-galacto-*heptitol* (**7e**). Ester **7b** [3,17,18] (500 mg, 2.25 mmol) was converted as described in g.p. 6 to afford **7e** (377 mg, 86%): mp 140 °C (from EtOH–MeOH), lit. 121–122 °C (hemihydrate) [18,23]; $[\alpha]_D$ +33.1°, lit. $[\alpha]_D^{20}$ +29.0° (*c* 1.92, H_2O) [18], lit. $[\alpha]_D^{20}$ +32.6° (*c* 1.32, H_2O) [23]; R_f (*s.s.* 3) 0.20; ^{1}H NMR (D_2O): δ 3.228 (ddd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.421 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.501 (dd, 1 H, $J_{4,5}$ 3.2 Hz, H-4), 3.516 (ddd, 1 H, $J_{6,7a}$ 8.2 Hz, $J_{6,7b}$ 3.9 Hz, H-6), 3.563 (dd, 1 H, $J_{1a,1b}$ −12.1 Hz, $J_{1a,2}$ 6.6 Hz, H-1a), 3.571 (dd, 1 H, H-7b), 3.631 (dd, 1 H, $J_{7a,7b}$ −11.6 Hz, H-7a), 3.786 (dd, 1 H, $J_{1b,2}$ 2.2 Hz, H-1b), 3.813 (dd, 1 H, $J_{5,6}$ 1.3 Hz, H-5); IR (KBr): ν 3400 (O–H), 1105, 1085, 1050, 1010 (C–O–C, C–O, C–C); CIMS: *m/z* (%) 389 (19), 195 (100), 177 (3), 159 (22), 141 (2), 123 (12). Anal. found: C, 43.21; H, 7.24.

2,6-Anhydro-meso-D-glycero-D-gulo-*heptitol* (**8e**). Ester **8b** [3,19] (500 mg, 2.25 mmol) was converted as described in g.p. 6 to give **8e** (388 mg, 89%): mp 199 °C (from aq EtOH), lit. 199–201 °C [24], lit. 203–205 °C [25], lit. 204–205 °C [26]; $[\alpha]_D$ 0 ± 0.1°, lit. $[\alpha]_D^{20}$ +3.1° (*c* 5.87, H_2O) [24], lit. $[\alpha]_D^{20}$ 0° (*c* 2, H_2O) [25], lit. $[\alpha]_D^{20}$ 0 ± 0.1° (*c* and solvent not indicated) [26]; R_f (*s.s.* 3) 0.30; ^{1}H NMR (D_2O): δ 3.219 (dd, 2 H, $J_{3,4} = J_{4,5}$ 8.9 Hz, H-3, H-5), 3.281 (ddd, 2 H, $J_{2,3} = J_{5,6}$ 9.8 Hz, H-2, H-6), 3.355 (dd, 1 H, H-4), 3.564 (dd, 2 H, $J_{1a,1b} = J_{7a,7b}$ −12.2 Hz, $J_{1a,2} = J_{6,7a}$ 5.9 Hz, H-1a, H-7a), 3.767 (dd, 2 H, $J_{1b,2} = J_{6,7b}$ 2.2 Hz, H-1b, H-7b); IR (KBr): ν 3450, 3260 (O–H), 1100, 1080, 1030, 1010 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 389 (57), 195 (100), 177 (5), 159 (34), 141 (7), 123 (18). Anal. found: C, 43.23; H, 7.26.

2,6-Anhydro-D-glycero-D-galacto-*heptitol* (**11e**). Ester **11b** [19,20] (500 mg, 2.25 mmol) was converted as described in g.p. 6 to give **11e** (381 mg, 87%): mp 141 °C (from aq EtOH), lit. 142–144 °C [27], lit. 129–130 °C [28]; $[\alpha]_D$ −33.5°, lit. $[\alpha]_D^{25}$ −33.6° (*c* 1.5, H_2O) [27], lit. $[\alpha]_D^{25}$ −33.4° (*c* 1.5, H_2O) [28]; R_f (*s.s.* 3) 0.20; ^{1}H NMR (D_2O): δ 3.228 (ddd, 1 H, $J_{6,7a}$ 6.6 Hz, $J_{6,7b}$ 2.2 Hz, H-6), 3.421 (dd, 1 H, $J_{5,6}$ 9.8 Hz, H-5), 3.501 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.516 (ddd, 1 H, $J_{2,3}$ 1.3 Hz, H-2), 3.563 (dd, 1 H, $J_{7a,7b}$ −12.1 Hz, H-7a), 3.571 (dd, 1 H, $J_{1b,2}$ 3.9 Hz, H-1b), 3.631 (dd, 1 H, $J_{1a,1b}$ −11.6 Hz, $J_{1a,2}$ 8.2 Hz, H-1a), 3.786 (dd, 1 H, H-7b), 3.813 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3); IR (KBr): ν 3400 (O–H), 1105, 1085, 1050, 1010 (C–O–C, C–O, C–C); CIMS: *m*/*z* (%) 389 (33), 195 (100), 177 (5), 159 (29), 141 (4), 123 (23). Anal. found: C, 43.15; H, 7.25.

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