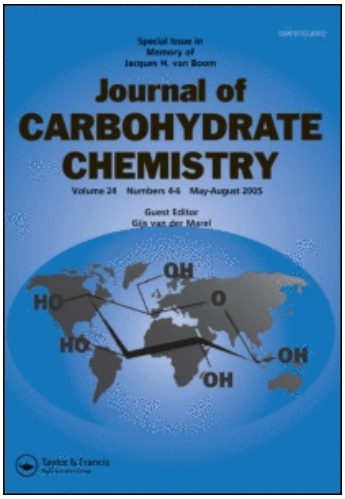

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Comprehensive Reinvestigation of The Reaction of D-Aldoses With Meldrum'S Acid Yielding Mainly Chain Extended 3,6-Anhydro-2-Deoxy-Aldono-1,4-Lactones

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COMPREHENSIVE REINVESTIGATION OF THE REACTION OF D-ALDOSES WITH MELDRUM'S ACID YIELDING MAINLY CHAIN EXTENDED 3,6-ANHYDRO-2-DEOXY-ALDONO-1,4-LACTONES

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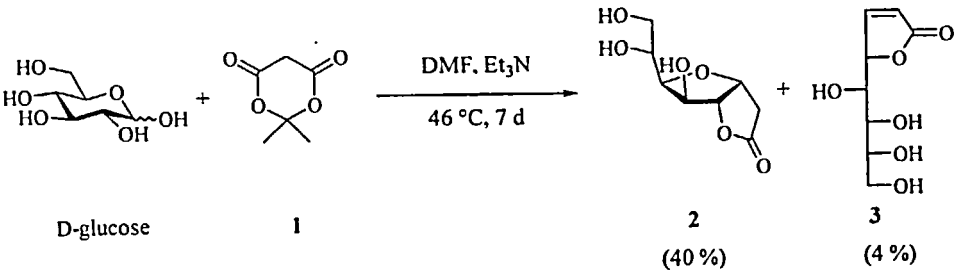
ABSTRACT

All diastereomeric *aldo*-D-pentoses and -D-hexoses were reacted with Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) under basic conditions. A protocol was applied and optimized which was originally reported by J. A. Galbis Perez *et al.* in 1990. In every case formal substitution of the anomeric hydroxyl against a carboxy-methylene group occurred thus elongating the carbon chain of the parent aldose by a C_2 fragment. Products are mainly 3,6-anhydro-2-deoxy-aldono-1,4-lactones in which the lactone rings are annulated to a furanoid system. However, D-mannose and D-lyxose also gave pyranoid 3,7-anhydro-1,4-lactones. Intermediates are unsaturated open-chain 1,4-lactones (butenolides) which in some cases could be isolated as by-products. Epimerisation at C-2 of the parent aldose occurred at least partially in most reactions. The products and their acetylated derivatives were characterized by ^1H and ^{13}C NMR spectroscopy. A proposed mechanism of this reaction is supported by additional experimental evidence.

INTRODUCTION

The formation of a C-C-bond at the anomeric centre of an aldose has been a challenging task for more than a century now. In most cases open-chain compounds were



Scheme 1. Reaction of D-Glucose with Meldrum's Acid (**1**)[3a]

obtained but there are also methods known which lead to so-called *C*-glycosides of furanoid or pyranoid structure. The relevant literature was reviewed recently.[1]

In connection with the latter item J. A. Galbis Perez *et al.* reported in 1986 an easy approach to *C*-glycosyl barbiturates through simple reaction of barbituric acid with an aldose.[2] Since Meldrum's acid, 2,2-dimethyl-1,3-dioxan-4,6-dione (**1**), has a very similar structure compared to barbituric acid, an analogous *C*-glycoside was expected. However, when these authors started to investigate this reaction in the early 1990's, 3,6-anhydro-1,4-lactone derivatives were obtained as the major products such as **2** from the reaction with D-glucose (Scheme 1).[3a] Compound **2** is formed by an intramolecular Michael addition of the unsaturated intermediate **3**. Analogous reactions were observed for D-xylose and D-galactose[3a] and L-arabinose and D-mannose, respectively.[3b] This initially surprising result can be explained by the high tendency of Meldrum's acid to lose acetone and carbon dioxide upon nucleophilic attack.[4]

These reports attracted our interest because of the great similarity of the annulated lactone structures with the cyclic carbamates of glycosylamines or glyco-oxazolidin-2-ones prepared by reaction of aldoses with potassium cyanate in water, which were studied by us in detail.[5] Thus, we expected product compositions corresponding to those found in their *N*-analogues. Since a divergent structure assigned by J. A. Galbiz Perez *et al.* to the main product obtained from the reaction of D-mannose with **1** was merely supported by incomplete analysis of vicinal coupling constants taken from 200 MHz ^{1}H NMR spectra[3b] we decided to comprehensively investigate/reinvestigate the behaviour of all diastereomeric *aldo*-D-pentoses and *aldo*-D-hexoses in the reaction with Meldrum's acid.

RESULTS AND DISCUSSION

Pentoses, D-arabinose, D-ribose, D-xylose, and D-lyxose, and hexoses, D-allose, D-altrose, D-galactose, D-talose, D-glucose, D-mannose, D-gulose, and D-idose, were first reacted with 1 equiv of Meldrum's acid for 10 days at 48 – 49 °C using 1 equiv of triethylamine as the base and *N,N*-dimethylformamide (DMF) as the solvent. Despite an increase of reaction time by three days and half the amount of solvent, these are almost the same conditions used by J. A. Galbis Perez *et al.*.[3] However, the results shown in parentheses in Tables 1 and 2 proved the conditions mentioned above as not optimal in every case considering conversion of the aldose. Therefore, we carefully varied the reaction conditions, including temperature, type of base, solvent, proportion of reactants, time, and even inert gas stripping, to establish the following conditions as the conditions of choice for the conversion of D-glucose as model aldose: *tert*-butylamine should be used as base, DMF as solvent, the reaction kept at 40 °C for 5 days, and the ratio of the reactants should be 1 equiv of aldose and base to 2 equiv of **1**. Tables 1 and 2 show the products received from the individual aldoses by applying these conditions.

The product mixtures obtained from these reactions were separated by column chromatography on silica gel, followed by further purification with charcoal. In some cases crystallization could be achieved from ethanol. When possible, products were characterized by mass spectrometry, elemental analysis (or high resolution mass spectrometry, alternatively), determination of the specific optical rotation and melting point (solids), as well as ^{1}H NMR and ^{13}C NMR spectroscopy, using two dimensional correlated spectroscopy in some cases. However, some by-products could not be isolated in pure form, thus allowing their characterization based only on NMR spectroscopic data.

In order to further support the structural assignments, the saturated bicyclic lactones were completely acetylated under standard basic conditions, yielding compounds **2a**, **5a**, **6a**, **9a**, **12a - 20a** (see Experimental). As expected, the ^{1}H NMR signals for H-5 and H-7 of fully acetylated furanoid structures are shifted considerably downfield in the ^{1}H NMR whereas in fully acetylated pyranoid structures the signals of the hydrogens at position 5 and 6 are found downfield compared to the unprotected compounds.

Additional support came from the comparison of the chemical shifts and coupling constants in the ^{1}H NMR and ^{13}C NMR spectra of the lactones and the corresponding *N*-

Table 1. Products of Reaction of *aldo*-D-Pentoses with Meldrum's Acid

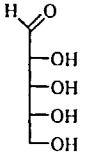
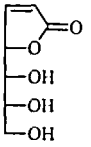
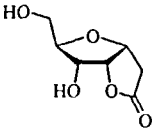
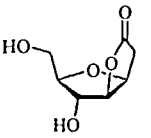
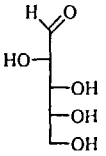
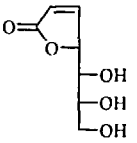
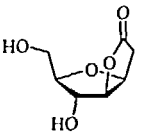
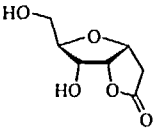
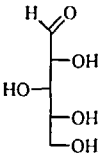
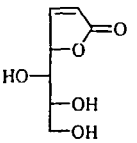
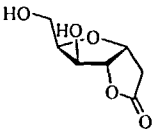
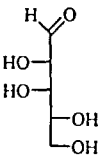
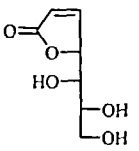
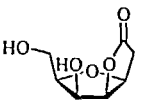
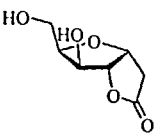
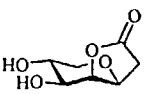
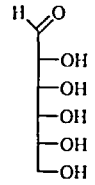
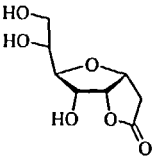
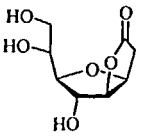
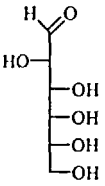
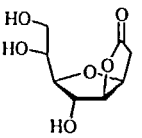
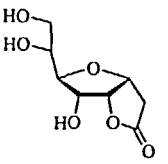
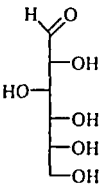
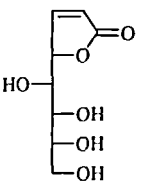
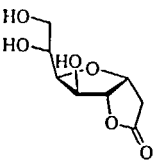
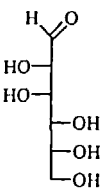
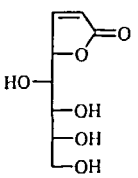
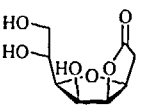
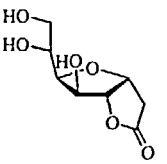
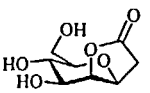
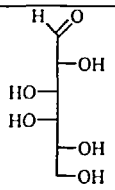
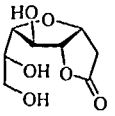
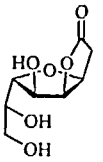
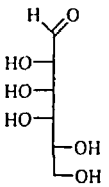
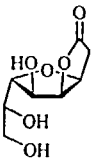
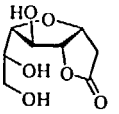
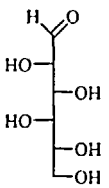
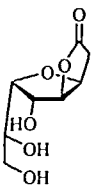
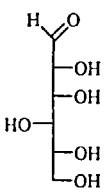
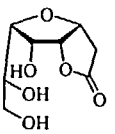
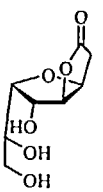
Pentose	Unsaturated Lactone	Furanoid Lactone without C-2 Epimerization	Furanoid Lactone with C-2 Epimerization	Pyranoid Lactone
				---
D-Ribose	**4**	**5**	**6**	
	5 % (5 %)	41 % (20 %)	21 % (61 %)	
		(Diacetate: **5a**)		
				---
D-Arabinose	**7**	**6**	**5**	
	6 % (6 %)	51 % (61 %)	20 % (15 %)	
[Lit.[3b] (L-enant.)	---	47 %	---	---]
		(Diacetate: **6a**)		
			---	---
D-Xylose	**8**	**9**		
	5 % (6 %)	67 % (63 %)		
[Lit.[3a]	4 %	57 %	---	---]
		(Diacetate: **9a**)		
				
D-Lyxose	**10**	**11**	**9**	**12**
	5 % (6 %)	5 % (3 %)	41 % (51 %)	10 % (22 %)
				(Diacetate: **12a**)

Table 2 – Part I. Products of Reaction of *aldo*-D-Hexoses with Meldrum's Acid

Hexose	Unsaturated Lactone	Furanoid Lactone without C-2 Epimerization	Furanoid Lactone with C-2 Epimerization	Pyranoid Lactone
 D-Allose	---	 **13** 31 % (20 %) (Triacetate: **13a**)	 **14** 51 % (61 %)	---
 D-Altrose	---	 **14** 91 % (81 %) (Triacetate: **14a**)	 **13** 0 % (10 %)	---
 D-Glucose	 **3** 0 % (0 %) 4 %	 **2** 91 % (41 %) 40 % (Triacetate: **2a**)	--- ---	--- ---]
 D-Mannose	 **3** 4 % (4 %) ---	 **15** 5 % (4 %) ---[6] (Triacetate: **15a**)	 **2** 36 % (41 %) 39 %	 **16** 15 % (12 %) 11 %[6]] (Triacetate: **16a**)

(continued)

Table 2 – Part II. Products of Reaction of *aldo*-D-Hexoses with Meldrum's Acid

Hexose	Unsaturated Lactone	Furanoid Lactone without C-2 Epimerization	Furanoid Lactone with C-2 Epimerization	Pyranoid Lactone
 D-Galactose	---	 **17** 56 % (60 %)	 **18** 30 % (15 %)	---
[Lit.[3a]	---	45 % (Triacetate: **17a**)	7 %	---]
 D-Talose	---	 **18** 67 % (30 %) (Triacetate: **18a**)	 **17** 22 % (29 %)	---
 D-Idose	---	 **19** 75 % (60 %) (Triacetate: **19a**)	---	---
 D-Gulose	---	 **20** 4 % (6 %) (Triacetate: **20a**)	 **19** 41 % (71 %)	---

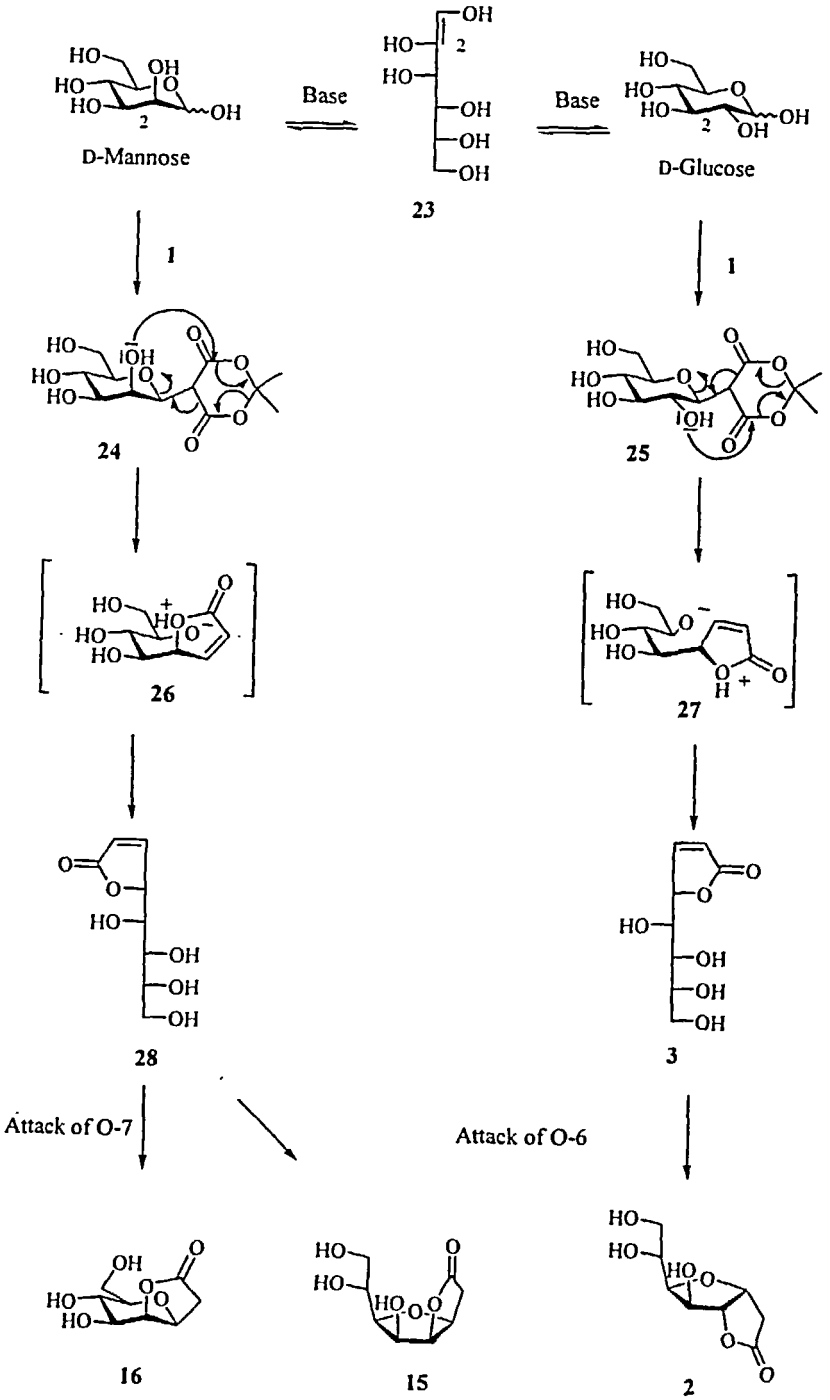
analogous cyclic carbamates for which two examples are given in tables 3-6.[5] This allowed a correction for the structure of **16** which was erroneously assumed to be the furanoid lactone **15**.[3b]

These results can be interpreted by assuming a Knoevenagel-Doebner reaction like J. A. Galbis Perez *et al.* suggested earlier.[3a] The following Scheme 2 illustrates the proposed mechanism with D-mannose as an example.

Primary nucleophilic attack by deprotonated **1** at the anomeric centre of the monosaccharide leads to C-glycoside **24** which can either be formed directly by a nucleophilic substitution of the anomeric hydroxyl group or in a two step sequence by nucleophilic addition to the acyclic *aldehydo*-D-glucose followed by intramolecular cyclic ether formation. However, we did not find any proof for an open chain adduct.

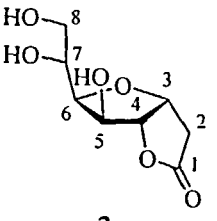
Since this reaction is obviously quite slow, C-2 epimerization of the monosaccharide in the sense of a Lobry de Bruyn-Alberda van Ekenstein rearrangement via enediol **23** can become a competing reaction under these conditions leading to a mixture of C-2 epimeric aldoses, D-mannose and D-glucose, and hence to a mixture of epimeric C-glycosides **24** and **25**. Thus, pentoses and hexoses can be grouped into pairs of C-2 epimers that in principle give rise to the same product spectrum with ratios depending on kinetic *vs* thermodynamic control. These pairs are D-arabinose and D-ribose, D-xylose and D-lyxose, D-glucose and D-mannose, D-galactose and D-talose, D-altrose and D-allose, and D-gulose and D-idose. Similar inversion of configuration at C-2 was observed in other cases in which unsaturated intermediates are encountered, for instance in other Knoevenagel-Doebner and Wittig reactions[1] or in the mentioned reaction of aldoses with potassium cyanate.[5] Usually, aldoses with a 2,4-*threo* configuration are less prone to this rearrangement because they lead directly to the favoured products. However, this tendency here is not as pronounced (compare Tables 1-2) as in the case in the reaction of aldoses with KOCN,[5] thus diminishing the preparative value of the investigated reaction in certain cases. Reaction products coming from the ketose D-fructose, which one would also expect to be present within the rearrangement equilibrium, were not found. We think this is due to the fact that ketoses are not reactive enough under these conditions to afford the desired transformation even when starting from pure D-fructose.

Subsequent loss of acetone and carbon dioxide from **24** and **25** give transients **26** and **27**, respectively, which lead to the unsaturated lactones **28** (not isolated) and **3** upon

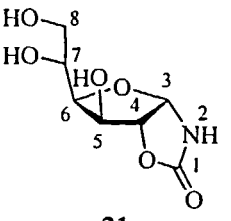


Scheme 2. Proposed Mechanism of the Reaction of Aldoses with Meldrum's Acid[3a]

Table 3. Comparison of NMR Spectroscopic Data of 3,6-Anhydro-2-deoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (**2**) with its *N*-Analogue 1-*N*,2-*O*-Carbonyl-α-D-glucofuranosylamine (**21**) - ^{1}H NMR Data[a,b]



2



21

	H-2	H-2'	H-3	H-4	H-5	H-6	H-7	H-8	H-8'
2	2.884	2.587	4.934	4.958	4.405	3.815	3.775	3.665	3.503
			$J_{3,4}$ 4.7	$J_{4,5}$ 0	$J_{5,6}$ 2.6	$J_{6,7}$ 8.8	$J_{7,8}$ 2.6	$J_{7,8'}$ 5.5	$J_{8,8'}$ -12.1
21	-	-	5.780	4.939	4.373	3.850	3.850	3.706	3.550
			$J_{3,4}$ 5.4	$J_{4,5}$ 0	$J_{5,6}$ 0	$J_{6,7}$ 8.7	$J_{7,8}$ 2.3	$J_{7,8'}$ 5.4	$J_{8,8'}$ -12.1

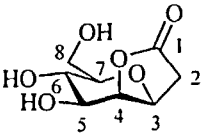
a. Spectra were recorded at 300.1 MHz in the case of **21**, and at 500.1 MHz for **2**, shifts are reported in ppm, selected coupling constants in Hz.
b. NMR data of **21** see ref. 5a.

Table 4. ^{13}C NMR Spectral Data for Compounds **2** and **21**[a,b]

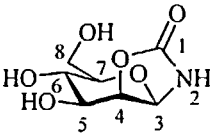
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
2	179.74	35.84	79.84	88.41	73.05	77.45	68.78	63.67
21	160.23	-	86.37	85.21	72.85	78.31	68.45	63.58

a. Spectra were recorded at 75.8 MHz in the case of **21** and at 125.8 MHz for **2**, shifts are reported in ppm.
b. NMR data of **21** see ref. 5a.

Table 5. Comparison of NMR Spectroscopic Data of 3,7-Anhydro-2-deoxy-D-*glycero*-D-*manno*-octono-1,4-lactone (**16**) with its *N*-Analogue 1-*N*.2-*O*-Carbonyl-β-D-mannopyranosylamine (**22**) - ^{1}H NMR[a,b]



16



22

	H-2	H-2'	H-3	H-4	H-5	H-6	H-7	H-8	H-8'
16	2.913	2.526	4.484	4.743	3.849	3.516	3.341	3.785	3.593
			$J_{3,4}$ 1.9	$J_{4,5}$ 4.0	$J_{5,6}$ 9.6	$J_{6,7}$ 9.7	$J_{7,8}$ 2.2	$J_{7,8'}$ 6.2	$J_{8,8'}$ -12.3
22	-	-	5.264	4.732	3.886	3.534	3.344	3.787	3.613
			$J_{3,4}$ 3.3	$J_{4,5}$ 4.7	$J_{5,6}$ 9.6	$J_{6,7}$ 9.4	$J_{7,8}$ 2.5	$J_{7,8'}$ 6.2	$J_{8,8'}$ -12.3

a. Spectra were recorded at 300.1 MHz, shifts are reported in ppm, selected coupling constants in Hz.
b. NMR data of **22** see ref. 5a.

Table 6. ^{13}C NMR Spectral Data for Compounds **16** and **22**[a,b]

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
16	179.29	38.18	73.84	82.75	71.48	66.90	78.38	60.99
22	160.96	-	81.31	79.53	70.56	67.12	75.32	60.96

a. Spectra were recorded at 75.8 MHz, shifts are reported in ppm.
b. NMR data of **22** see ref. 5a.

intramolecular hydrogen transfer. Finally, intramolecular Michael addition establishes the furanoid and pyranoid lactones by attack of the hydroxyl group at position 6 or 7, respectively.

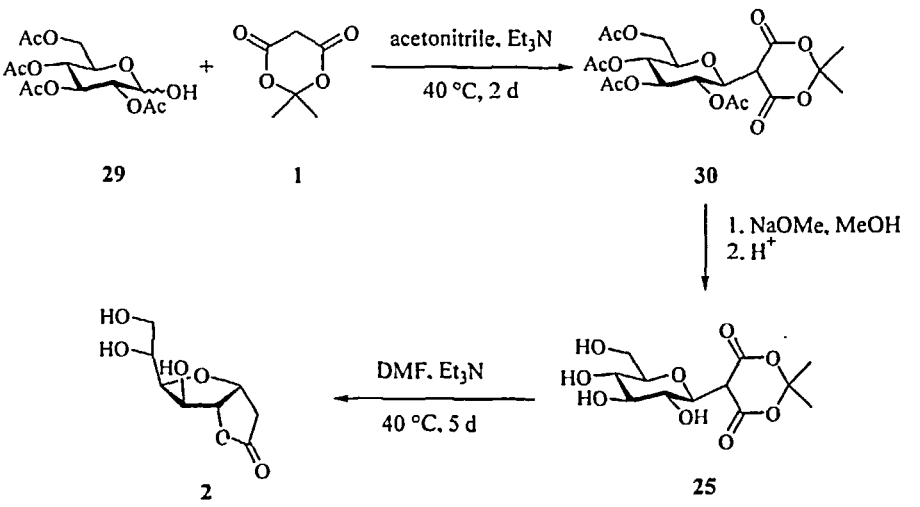
The proposed mechanism is further confirmed by the fact that the reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (**29**) with **1** gave **30**.[3b] Deprotection and treatment of the unprotected compound **25** with DMF and triethylamine lead to the expected formation of **2** (Scheme 3) as the unsaturated lactone (butenolide) **3** does when heated in DMF in presence of base, thus confirming the role of these intermediates.

The observed proportion of the products obviously depends on the steric demand of the final products with the furanoid 3,6-anhydrides dominating over the 3,7-analogues, probably for kinetic reasons. Therefore, sterically very crowded products like **11**, **15**, or **20** are only observed in cases where no epimerization of the parent aldose's configuration is necessary to obtain it but not in the case of its C-2 epimeric "sister" aldose.

The generally disadvantaged pyranoid 3,7-anhydro-1,4-lactones are formed only in these latter cases. In fact, only two pyranoid products, **12** and **16**, derived from D-lyxose and D-mannose, were obtained at all. From our experience with the reaction of aldoses with KOCN we would have expected such a product in case of D-gulose, too, which also establishes the extremely unfavourable 2,3,4-*lyxo* configuration, but it was not detected.

EXPERIMENTAL

General Remarks. All solvents were purified by standard procedures. D-arabinose, D-ribose, D-xylose, D-lyxose, D-glucose, D-galactose and D-mannose were used as purchased. D-allose, D-altrose, D-gulose, D-idose, and D-talose were prepared from D-glucose, D-xylose, and D-galactose, respectively, following literature procedures. Thin-layer chromatography was performed on aluminium TLC-layers Silica gel 60 F_{254} from Merck. Detection was done by treating with 10 % sulphuric acid and heating with a heat-gun. Products were purified by column chromatography on silica gel 60 (70 – 230 mesh) from Merck. NMR spectra were recorded on a Bruker AM 300 (^{1}H NMR = 300.1; ^{13}C NMR = 75.8 MHz) or on a Bruker AMX R 500 (^{1}H NMR = 500.1; ^{13}C NMR = 125.8



29 1 30

2 25

Scheme 3

MHz). Chemical shifts are reported on the δ-scale [ppm] relative to residual nondeuterated solvent or acetone signals in D_2O or $CDCl_3$ as internal standards. Mass spectra were taken on a Finnigan MAT 212 with data system SS 300 or on a Finnigan MAT 95 with data system DEC-Station 5000 using chemical ionization with *iso*-butane as reactant gas. Microanalyses were carried out on a Carlo Erba 1104 or on a Fison Instruments EA 1108. Melting points were determined with a hot-stage microscope SM-Lux from Leitz and are not corrected. Specific optical rotations were measured on a Perkin Elmer Polarimeter 241 MC or 343 in a 1 dm cell.

General Procedure 1 for the Reaction of Pentoses and Hexoses with Meldrum's Acid (Standard Conditions). 3.17 g (22 mmol) of 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid) were dissolved in 15 mL of *N,N*-dimethylformamide and 1 equiv of aldose (3.3 g of pentose or 4.0 g of hexose) and 3.6 mL (1 equiv) of triethylamine were added. The resulting mixture was heated to 48 - 49 °C for 10 days.[3a] The crude reaction mixture was obtained by evaporation of the solvent. The individual products were isolated by column chromatography on silica gel using ethyl acetate / ethanol / water (14/4/1 v/v/v) as the eluent and further purified by treatment with charcoal. In most cases crystallization was successful from ethanol.

General Procedure 2 for the Reaction of Pentoses and Hexoses with Meldrum's Acid (Optimized Conditions for the Formation of 2). 6.4 g (44 mmol) of **1** were dissolved in 30 mL of *N,N*-dimethylformamide. 0.5 Equiv of aldose (3.3 g of pentose or 4.0 g of hexose) and 2.4 mL (0.5 equiv) of *tert*-butylamine were added. The resulting mixture was heated to 40 °C for 5 days. The workup was done analogous to the reaction under standard conditions.

General Acetylation Procedure. Unprotected sugar lactones were dissolved in a mixture of acetic anhydride and pyridine. Approx 8 mL of pyridine and 5 mL of acetic anhydride were used per 1 g of lactone and OH-function. After twelve hours the reaction was normally completed and the solution was concentrated to dryness with the help of toluene. The residue was treated with charcoal. Crystallization could be done from cold ethanol in some cases.

Reaction of D-Ribose and D-Arabinose with Meldrum's Acid. D-Ribose yielded 2.35 g (41 %) 3,6-anhydro-2-deoxy-D-*gluco*-heptono-1,4-lactone (**6**), 0.78 g (20 %) 3,6-anhydro-2-deoxy-D-*altro*-heptono-1,4-lactone (**5**), and 0.210 g (5 %) 2,3-dideoxy-D-*ribo*-hept-2-enono-1,4-lactone (**4**) when general procedure 1 was applied and 0.80 g (21 %) **6**, 1.57 g (41 %) **5**, and 0.210 g (5 %) **4** after treatment with Meldrum's acid following general procedure 2. D-Arabinose gave 2.35 g (61 %) **6** [Lit. (L-enantiomer): [3b] 47 %], 0.59 g (15 %) **5**, and 0.212 g (6 %) 2,3-dideoxy-D-*arabino*-hept-2-enono-1,4-lactone (**7**) when treated according to general procedure 1. When general procedure 2 was employed 1.97 g (51 %) **6**, 0.78 g (20 %) **5**, and 0.215 g (6 %) **7** were obtained.

2,3-Dideoxy-D-*ribo*-hept-2-enono-1,4-lactone (4). **4** was not obtained in pure form. Thus only its TLC *Rf* value and its ^{13}C NMR data could unambiguously be determined: TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.68; ^{13}C NMR (75.8 MHz, D_2O) δ 177.01 (C-1), 157.77 (C-3), 121.74 (C-2), 84.66 (C-4), 71.61 (C-5), 69.45 (C-6), 62.97 (C-7).

3,6-Anhydro-2-deoxy-D-*altro*-heptono-1,4-lactone (5). **5** was obtained as a syrup: $[\alpha]_D^{20}$ +117° (*c* 1.3, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.61; ^1H NMR (300.1 MHz, D_2O) δ 5.037 (dd, 1 H, $^3J_{3,4}$ 5.0 Hz, $^3J_{4,5}$ 4.4 Hz, H-4), 4.849 (dd, 1 H, $^3J_{2a,3}$ 6.6 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.164 (dd, 1 H, $^3J_{5,6}$ 8.8 Hz, H-5), 3.803 (ddd, 1 H, $^3J_{6,7a}$ 2.8 Hz, $^3J_{6,7b}$ 5.0 Hz, H-6), 3.715 (dd, 1 H, $^2J_{7a,7b}$ -13.1 Hz, H-7a), 3.558 (dd, 1 H,

H-7b), 2.948 (dd, 1 H, $^2J_{2a,2b}$ -19.2 Hz, H-2a), 2.618 (d, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.72 (C-1), 84.66 (C-4), 80.59 (C-3), 76.73 (C-6), 71.05 (C-5), 60.45 (C-7), 36.95 (C-2); MS (CI, *iso*-butane): *m/z* (%) 175 (100) [MH^+]. HRMS (CI, *iso*-butane): Calcd for $C_7H_{11}O_5^+$: 175.0606. Found: 175.0517.

5,7-Di-*O*-acetyl-3,6-anhydro-2-deoxy-D-*altro*-heptono-1,4-lactone (5a). Standard acetylation of **5** gave **5a** as a syrup: $[\alpha]_D^{20}$ +181.5° (*c* 1.6, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.43; ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 5.097 (dd, 1 H, $^3J_{3,4}$ 5.1 Hz, $^3J_{4,5}$ 4.5 Hz, H-4), 4.856 (dd, 1 H, $^3J_{5,6}$ 8.2 Hz, H-5), 4.831 (dd, 1 H, $^3J_{2a,3}$ 6.4 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.229 (dd, 1 H, $^3J_{6,7a}$ 3.2 Hz, $^2J_{7a,7b}$ -12.1 Hz, H-7a), 4.098 (ddd, 1 H, $^2J_{6,7b}$ 5.1 Hz, H-6), 4.001 (dd, 1 H, H-7b), 2.737 (dd, 1 H, $^2J_{2a,2b}$ -19.0 Hz, H-2a), 2.579 (d, 1 H, H-2b), 2.028 (s, 3 H, CH_3), 1.976 (s, 3 H, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 174.60 (C-1), 170.18, 169.83 (2 × CH_3CO_2), 80.07 (C-4), 76.70 (C-3), 76.65 (C-6), 72.79 (C-5), 62.56 (C-7), 36.08 (C-2), 20.40, 20.16 (2 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 259 (100) [MH^+].

Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46. Found: C, 51.63; H, 5.39.

3,6-Anhydro-2-deoxy-D-*gluco*-heptono-1,4-lactone (6).[3b] **6** could only be isolated as a syrup: $[\alpha]_D^{20}$ -27.5 ° (*c* 1.6, water) [Lit. (L-enantiomer):[3b] +10 ° (*c* 1, water)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.74; ^{1}H NMR (300.1 MHz, D_2O) δ 4.923 (d, 1 H, $^3J_{3,4}$ 4.4 Hz, $^3J_{4,5}$ 0 Hz, H-4), 4.862 (dd, 1 H, $^3J_{2a,3}$ 5.5 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.208 (d, 1 H, $^3J_{5,6}$ 5.5 Hz, H-5), 3.853 (ddd, 1 H, $^3J_{6,7a}$ 3.3 Hz, $^3J_{6,7b}$ 5.5 Hz, H-6), 3.686 (dd, 1 H, $^2J_{7a,7b}$ -12.1 Hz, H-7a), 3.541 (dd, 1 H, H-7b), 2.894 (dd, 1 H, $^2J_{2a,2b}$ -19.3 Hz, H-2a), 2.628 (d, 1 H, H-2b) [Lit. (L-enantiomer):[3b] (200 MHz, DMSO-d_6) 5.66 (d, 1 H, $^3J_{5,OH}$ 4.8 Hz, OH-5), 4.85 (t, 1 H, $^3J_{7,OH}$ 5.2 Hz, OH-7), 4.76 (dd, 1 H, $^3J_{3,4}$ 4.4 Hz, $^3J_{4,5}$ 1.1 Hz,H-4), 4.69 (dd, 1 H, $^3J_{2a,3}$ 5.4 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.02 (dd, 1 H, $^3J_{5,6}$ 4.6 Hz, H-5), 3.67 (td, 1 H, $^3J_{6,7a}$ 5.5 Hz, $^3J_{6,7b}$ 5.5 Hz, H-6), 3.60 – 3.30 (m, 2 H, H-7a and H-7b), 2.85 (dd, 1 H, $^2J_{2a,2b}$ –18.2 Hz, H-2a), 2,45 (d, 1 H, H-2b)]; ^{13}C NMR (75.8 MHz, D_2O) δ 179.21 (C-1), 90.98 (C-4), 86.47 (C-3), 78.08 (C-6), 75.53 (C-5), 61.24 (C-7), 36.23 (C-2) [Lit. (L-enantiomer):[3b] (20.15 MHz, DMSO-d_6) 175.2 (C-1), 89.9, 87.1, 76.9, 75.4 (C-3, C-4, C-5, and C-6), 61.2 (C-7), 35.8 (C-2)]; MS (CI, *iso*-butane): *m/z* (%) 175 (100) [MH^+].

Anal. Calcd for $C_7H_{10}O_5$ (174.15): C, 48.28; H, 5.79. Found: C, 47.93; H, 6.08.

5,7-Di-*O*-acetyl-3,6-anhydro-2-deoxy-D-*gluco*-heptono-1,4-lactone (6a).[3b]

Standard acetylation of **6** afforded **6a** as a syrup: $[\alpha]_D^{20}$ -69.7 ° (*c* 1.4, chloroform) [Lit. (L-enantiomer):[3b] +86 (*c* 1, chloroform)]; TLC (methyl *tert*-butyl ether) R_f 0.44; ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 5.117 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.2 Hz, H-5), 4.831 (d, 1 H, $^3J_{3,4}$ 3.8 Hz, H-4), 4.785 (dd, 1 H, $^3J_{2a,3}$ 5.1 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.261 (dd, 1 H, $^3J_{6,7a}$ 3.2 Hz, $^2J_{7a,7b}$ -11.4 Hz, H-7a), 4.120 (dd, 1 H, $^3J_{6,7b}$ 5.1 Hz, H-7b), 4.072 (ddd, 1 H, H-6), 2.689 (dd, 1 H, $^2J_{2a,2b}$ -18.4 Hz, H-2a), 2.635 (d, 1 H, H-2b), 2.043 (s, 3 H, CH_3), 1.993 (s, 3 H, CH_3) [Lit. (L-enantiomer):[3b] (200 MHz, $CDCl_3$) 5.21 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.9 Hz, H-5), 4.98 – 4.78 (m, 2 H, H-3 and H-4), 4.40 – 4.10 (m, 1 H, H-6), 4.38 (dd, 1 H, $^3J_{6,7a}$ 5.1 Hz, $^2J_{7a,7b}$ –12.7 Hz, H-7a), 4.18 (dd, 1 H, $^3J_{6,7b}$ 4.1 Hz, H-7b), 2.74 (m, 2 H, H-2a and H-2b), 2.13, 2.08 (2s, 6 H, 2 × CH_3)]; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 173.99 (C-1), 170.46, 169.50 (2 × CH_3CO_2), 86.82 (C-4), 83.11 (C-3), 78.14 (C-6), 77.49 (C-5), 63.03 (C-7), 35.80 (C-2), 20.42, 20.39 (2 × CH_3) [Lit. (L-enantiomer):[3b] (20.15 MHz, $CDCl_3$) 173.8 (C-1), 170.3, 169.4 (2 × CH_3CO_2), 86.9 (C-4), 83.2 (C-6), 78.2 (C-3), 77.7 (C-5), 63.1 (C-7), 35.8 (C-2), 20.3 ((2 × CH_3)]; MS (CI, *iso*-butane): *m/z* (%) 259 (100) [MH^+].

Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46, found C, 51.65; H, 5.43.

2,3-Dideoxy-D-*arabino*-hept-2-enono-1,4-lactone (7). **7** could not be isolated as a pure compound. Therefore, only its TLC *Rf* value and its ^{13}C NMR data could unambiguously be determined: TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.65; ^{13}C NMR (75.8 MHz, D_2O) δ 176.81 (C-1), 156.01 (C-3), 122.34 (C-2), 85.76 (C-4), 72.13 (C-5), 70.21 (C-6), 62.94 (C-7).

Reaction of D-Xylose and D-Lyxose with Meldrum's Acid). 2.43 g (63 %) 3,6-Anhydro-2-deoxy-D-*ido*-heptono-1,4-lactone (**9**) and 0.213 g (6 %) 2,3-dideoxy-D-*xylo*-hept-2-enono-1,4-lactone (**8**) were obtained from D-xylose [Lit.:[3a] 57 % and 4 %, respectively], when treated according to general procedure 1. When general procedure 2 was employed 2.55 g (67 %) **9** and 0.210 g (5 %) **8** were obtained. D-Lyxose gave 1.97 g (51 %) **9**, 0.12 g (3 %) 3,6-anhydro-2-deoxy-D-*galacto*-heptono-1,4-lactone (**11**), 0.86 g (22 %) 3,7-anhydro-2-deoxy-D-*lyxo*-heptono-1,4-lactone (**12**), and 0.216 g (6 %) 2,3-dideoxy-D-*lyxo*-hept-2-enono-1,4-lactone (**10**) when general procedure 1 was used and 1.57 g (41 %) **9**, 0.21 g (5 %) **11**, 0.39 g (10 %) **12**, and 0.209 g (5 %) **10** after treatment with Meldrum's acid following general procedure 2.

2,3-Dideoxy-D-*xylo*-hept-2-enono-1,4-lactone (8).[3a] **8** was still contaminated with the other products. Therefore, only the TLC *Rf* value and the NMR data could be

assigned unambiguously: TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.67; ^{1}H NMR (500.1 MHz, D_2O) δ 7.618 (dd, 1 H, $^3J_{2,3}$ 5.7 Hz, $^3J_{3,4}$ 1.9 Hz, H-3), 6.112 (dd, 1 H, $^4J_{2,4}$ 1.9 Hz, H-2), 5.232 (ddd, 1 H, $^3J_{4,5}$ 3.8 Hz, H-4), 3.770 (dd, 1 H, $^3J_{5,6}$ 4.4 Hz, H-5), 3.685 (ddd, 1 H, $^3J_{6,7a}$ 4.5 Hz, $^3J_{6,7b}$ 6.4 Hz, H-6), 3.582 (dd, 1 H, $^2J_{7a,7b}$ -12.0 Hz, H-7a), 3.528 (dd, 1 H, H-7b) [Lit.:[3a] (80.1 MHz, D_2O): δ 7.77 (dd, 1 H, $^3J_{2,3}$ 5.8 Hz, $^3J_{3,4}$ 1.5 Hz, H-3), 6.15 (dd, 1 H, $^4J_{2,4}$ 1.9 Hz, H-2), 5.21 (ddd, 1 H, $^3J_{4,5}$ 5.4 Hz, H-4), 4.00 – 3.40 (m, 4 H, H-5, H-6, H-7a, and H-7b)]; ^{13}C NMR (125.8 MHz, D_2O) δ 176.80 (C-1), 156.99 (C-3), 121.68 (C-2), 85.57 (C-4), 72.26 (C-5), 70.84 (C-6), 62.54 (C-7).

3,6-Anhydro-2-deoxy-D-*ido*-heptono-1,4-lactone (9).[3a] **9** was obtained as a syrup: $[\alpha]_D^{20}$ +28.0° (*c* 1.2, water) [Lit.:[3a] +23.0° (*c* 0.5, water)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.76; ^{1}H NMR (300.1 MHz, D_2O) δ 4.971 (dd, 1 H, $^3J_{2a,3}$ 6.1 Hz, $^3J_{2b,3}$ = 0 Hz, $^3J_{3,4}$ 3.9 Hz, H-3), 4.971 (d, 1 H, $^3J_{4,5}$ 0 Hz, H-4), 4.392 (d, 1 H, $^3J_{5,6}$ 3.3 Hz, H-5), 4.028 (ddd, 1 H, $^3J_{6,7a}$ 4.4 Hz, $^3J_{6,7b}$ 7.1 Hz, H-6), 3.760 (dd, 1 H, $^2J_{7a,7b}$ -11.5 Hz, H-7a), 3.654 (dd, 1 H, H-7b), 2.922 (dd, 1 H, $^2J_{2a,2b}$ -19.2 Hz, H-2a), 2.608 (d, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.64 (C-1), 88.90 (C-4), 81.13 (C-3), 77.07 (C-6), 73.45 (C-5), 59.73 (C-7), 35.87 (C-2). [Lit.:[3a] (20.15 MHz, D_2O) δ 180.2 (C-1), 89.8* (C-4), 82.0* (C-6), 77.9* (C-3), 74.5* (C-5), 60.6 (C-7), 36.7 (C-2), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 175 (100) [MH^+].

Anal. Calcd for $C_7H_{10}O_5$ (174.15): C, 48.28; H, 5.79. Found: C, 47.45; H, 6.03.

5,7-Di-*O*-acetyl-3,6-anhydro-2-deoxy-D-*ido*-heptono-1,4-lactone (9a).[3a] Standard acetylation of **9** afforded **9a** as colourless crystals: mp 61-63 °C [Lit.:[3a] 61-62 °C (ethanol)]; $[\alpha]_D^{20}$ +58.5° (*c* 1.2, chloroform) [Lit.:[3a] +59° (*c* 0.5, chloroform)]; TLC (methyl *tert*-butyl ether) R_f 0.45; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.464 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.9 Hz, H-5), 4.968 (ddd, 1 H, $^3J_{2a,3}$ 5.5 Hz, , $^3J_{2b,3}$ 1.7 Hz, $^3J_{3,4}$ 3.9 Hz, H-3), 4.886 (d, 1 H, H-4), 4.375 (ddd, 1 H, $^3J_{6,7a}$ 4.4 Hz, $^3J_{6,7b}$ 7.2 Hz, H-6), 4.220 (dd, 1 H, $^2J_{7a,7b}$ -11.5 Hz, H-7a), 4.152 (dd, 1 H, H-7b), 2.771 (dd, 1 H, $^2J_{2a,2b}$ -18.7 Hz, H-2a), 2.684 (dd, 1 HH-2b), 2.102 (s, 3 H, CH_3), 2.052 (s, 3 H, CH_3) [Lit.:[3a] (200 MHz, $CDCl_3$) δ 5.31 (bd, 1 H, $^3J_{4,5}$ 0.8 Hz, $^3J_{5,6}$ 3.7 Hz, H-5), 4.85 (td, 1 H, $^3J_{2a,3}$ 5.5 Hz, $^3J_{2b,3}$ 1.5 Hz, $^3J_{3,4}$ 4.6 Hz, H-3), 4.77 (bd, 1 H, H-4), 4.24 (m, 1 H, $^3J_{6,7a}$ 4.7 Hz, $^3J_{6,7b}$ 7.0 Hz, H-6), 4.09 (dd, 1 H, $^2J_{7a,7b}$ -11.7 Hz, H-7a), 4.00 (dd, 1 H, H-7b), 2.67 (dd, 1 H, $^2J_{2a,2b}$ -18.9 Hz, H-2a), 2.52 (dd, 1 H, H-2b), 1.97 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3)]; ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.32 (C-1), 170.35, 169.23 (2 × CH_3CO_2), 85.37 (C-4), 77.32 (C-3),

76.99 (C-6), 75.10 (C-5), 61.39 (C-7), 35.59 (C-2), 20.62, 20.45 (2 × CH_3) [Lit.:[3a] (20.15 MHz, $CDCl_3$) δ 174.2 (C-1), 170.2, 169.1 (2 × CH_3CO_2), 85.5 (C-4)*, 77.4 (C-3)*, 77.0 (C-5)*, 75.2 (C-6)*, 61.3 (C-7), 35.5 (C-2), 20.4, 20.3 (2 × CH_3), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 259 (100) [MH^+].

Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46. Found: C, 52.06; H, 5.35.

2,3-Dideoxy-D-*lyxo*-hept-2-enono-1,4-lactone (10). **10** was still contaminated with the other products. Therefore, only the TLC *Rf* value and the ^{13}C NMR data could be assigned unambiguously: TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.68; ^{13}C NMR (125.8 MHz, D_2O) δ 176.54 (C-1), 157.53 (C-3), 121.72 (C-2), 85.22 (C-4), 71.38 (C-5), 70.90 (C-6), 62.67 (C-7).

3,6-Anhydro-2-deoxy-D-*galacto*-heptono-1,4-lactone (11). **11** was obtained as a syrup: TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.66; ^1H NMR (300.1 MHz, D_2O) δ 5.098 (dd, 1 H, $^3J_{3,4}$ 5.8 Hz, $^3J_{4,5}$ 5.5 Hz, H-4), 4.692 (ddd, 1 H, $^3J_{2a,3}$ 7.2 Hz, $^3J_{2b,3}$ 1.9 Hz, H-3), 4.499 (dd, 1 H, $^3J_{5,6}$ 1.1 Hz, H-5), 3.962 (ddd, 1 H, $^3J_{6,7a}$ 3.9 Hz, $^3J_{6,7b}$ 7.7 Hz, H-6), 3.760 (dd, 1 H, $^2J_{7a,7b}$ -12.0 Hz, H-7a), 3.598 (dd, 1 H, H-7b), 2.926 (dd, 1 H, $^2J_{2a,2b}$ -19.0 Hz, H-2a), 2.639 (dd, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.72 (C-1), 84.39 (C-4), 82.38 (C-6), 76.60 (C-3), 70.87 (C-5), 60.29 (C-7), 36.21 (C-2): MS (CI, *iso*-butane): *m/z* (%) 175 (100) [MH^+]. HRMS (CI, *iso*-butane) Calcd for $C_7H_{11}O_5^+$: 175.0606. Found: 175.0855.

3,7-Anhydro-2-deoxy-D-*galacto*-heptono-1,4-lactone (12). **12** was obtained as crystalline material: mp 189–191 °C (ethanol); $[\alpha]_D^{20}$ -159.7° (*c* 1.3, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.64; ^1H NMR (500.1 MHz, D_2O) δ 4.660 (dd, 1 H, $^3J_{3,4}$ 1.9 Hz, $^3J_{4,5}$ 4.5 Hz, H-4), 4.372 (dd, 1 H, $^3J_{2a,3}$ 4.5 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 3.725 (dd, 1 H, $^3J_{6,7a}$ 5.1 Hz, $^2J_{7a,7b}$ -11.4 Hz, H-7a), 3.709 (dd, 1 H, $^3J_{5,6}$ 9.6 Hz, H-5), 3.639 (ddd, 1 H, $^3J_{6,7b}$ 10.2 Hz, H-6), 3.122 (dd, 1 H, H-7b), 2.837 (dd, 1 H, $^2J_{2a,2b}$ -17.8 Hz, H-2a), 2.410 (d, 1 H, H-2b); ^{13}C NMR (125.8 MHz, D_2O) δ 179.13 (C-1), 82.71 (C-4), 74.59 (C-3), 71.53 (C-5), 67.89 (C-6), 66.31 (C-7), 38.13 (C-2); MS (CI, *iso*-butane): *m/z* (%) 175 (100) [MH^+].

Anal. Calcd for $C_7H_{10}O_5$ (174.15): C, 48.28; H, 5.79. Found: C, 47.84; H, 5.81.

5,6-Di-*O*-acetyl-3,7-anhydro-2-deoxy-D-*galacto*-heptono-1,4-lactone (12a). Standard acetylation of **12** returned **12a** as colourless crystals: mp 157-159 °C (ethanol); $[\alpha]_D^{20}$ -196.6° (*c* 1.1, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.41; ^1H NMR (500.1

MHz, $CDCl_3$) δ 5.116 (ddd, 1 H, $^3J_{5,6}$ 10.2 Hz, $^3J_{6,7a}$ 4.5 Hz, $^3J_{6,7b}$ 9.5 Hz, H-6), 5.075 (dd, 1 H, $^3J_{4,5}$ 3.8 Hz, H-5), 4.708 (dd, 1 H, $^3J_{3,4}$ 1.9 Hz, H-4), 4.342 (dd, 1 H, $^3J_{2a,3}$ 3.8 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 3.982 (dd, 1 H, $^2J_{7a,7b}$ -11.4 Hz, H-7a), 3.245 (dd, 1 H, H-7b), 2.642 (dd, 1 H, $^2J_{2a,2b}$ -17.2 Hz, H-2a), 2.523 (d, 1 H, H-2b), 2.057 (s, 3 H, CH_3), 1.980 (s, 3 H, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 173.95 (C-1), 170.32, 169.58 (2 × CH_3CO_2), 77.79 (C-4), 73.72 (C-3), 70.40 (C-5), 65.75 (C-6), 65.42 (C-7), 37.43 (C-2), 20.57, 20.54 (2 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 259 (85) [MH^+], 199 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{11}H_{14}O_7$ (258.23): C, 51.16; H, 5.46: Found: C, 51.48; H, 4.91.

Reaction of D-Allose and D-Altrose with Meldrum's Acid). 0.92 g (20 %) 3,6-Anhydro-2-deoxy-D-*glycero*-D-*altro*-octono-1,4-lactone (**13**) and 2.76 g (61 %) 3,6-anhydro-2-deoxy-D-*glycero*-D-*gluco*-octono-1,4-lactone (**14**) were received from D-allose when treated according to general procedure 1. When general procedure 2 was used 31 % (1.41 g) **13**, and 51 % (2.31 g) **14** were obtained. D-Altrose gave 0.46 g (10 %) **13** and 3.68 g (81 %) **14** when general procedure 1 was employed and 4.14 g (91 %) **14** as a single product after treatment with Meldrum's acid following general procedure 2.

3,6-Anhydro-2-deoxy-D-*glycero*-D-*altro*-octono-1,4-lactone (13). **13** was obtained as colourless crystals: mp 127-129 °C (ethanol); $[\alpha]_D^{20}$ +114.2° (*c* 1.6, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.52; ^1H NMR (300.1 MHz, D_2O) δ 4.840 (d, 1 H, $^3J_{3,4}$ 4.5 Hz, $^3J_{4,5}$ 0 Hz, H-4), 4.785 (dd, 1 H, $^3J_{2a,3}$ 5.1 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.334 (d, 1 H, $^3J_{5,6}$ 4.5 Hz, H-5), 3.717 (dd, 1 H, $^3J_{6,7}$ 5.7 Hz, H-6), 3.606 (ddd, 1 H, $^3J_{7,8a}$ 3.8 Hz, $^3J_{7,8b}$ 7.0 Hz, H-7), 3.533 (dd, 1 H, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 3.404 (dd, 1 H, H-8b), 2.814 (dd, 1 H, $^2J_{2a,2b}$ -19.1 Hz, H-2a), 2.554 (d, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.16 (C-1), 91.10 (C-4), 86.60 (C-3), 78.26 (C-6), 75.12 (C-5), 71.31 (C-7), 62.69 (C-8), 36.33 (C-2); MS (CI, *iso*-butane): *m/z* (%) 205 (95) [MH^+], 169 (100) [MH^+-$2H_2O$]; HRMS (CI, *iso*-butane) Calcd for $C_8H_{13}O_6^+$: 205.0712. Found: 205.0658.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-D-*altro*-octono-1,4-lactone (13a). Acetylation of **13** afforded **13a** as a syrup: $[\alpha]_D^{20}$ -165.1° (*c* 1.3, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.48; ^1H NMR (500.1 MHz, $CDCl_3$) δ 5.379 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 4.5 Hz, H-5), 5.183 (ddd, 1 H, $^3J_{6,7}$ 5.1 Hz, $^3J_{7,8a}$ 3.8 Hz, $^3J_{7,8b}$ 5.7 Hz, H-7), 4.777 (d, 1 H, $^3J_{3,4}$ 2.5 Hz, H-4), 4.773 (dd, 1 H, $^3J_{2a,3}$ 4.5 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.313 (dd, 1 H, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 4.076 (dd, 1 H, H-6), 4.044 (dd, 1 H, H-8b), 2.691 (dd, 1 H, $^2J_{2a,2b}$ -17.8 Hz, H-2a), 2.634 (d, 1 H, H-2b), 2.071 (s, 3 H, CH_3), 2.016 (s, 3 H, CH_3),

1.993 (s, 3 H, CH_3); ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 173.74 (C-1), 170.28, 169.87, 169.21 (3 × CH_3CO_2), 87.07 (C-4), 83.63 (C-3), 78.11 (C-6), 76.53 (C-5), 69.73 (C-7), 61.97 (C-8), 35.70 (C-2), 2 × 20.57, 20.47 (3 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 331 (4) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.91; H, 5.52.

3,6-Anhydro-2-deoxy-D-*glycero*-D-*gluco*-octono-1,4-lactone (14). **14** was obtained as colourless crystals: mp 127–130 °C (ethanol); $[\alpha]_D^{20}$ -121.6 ° (*c* 1.1, water); TLC (methyl *tert*-butyl ether) R_f 0.46; ^1H NMR (500.1 MHz, D_2O) δ 5.063 (dd, 1 H, $^3J_{3,4}$ 4.4 Hz, $^3J_{4,5}$ 4.4 Hz, H-4), 4.868 (ddd, 1 H, $^3J_{2a,3}$ 6.6 Hz, $^3J_{2b,3}$ 1.1 Hz, H-3), 4.381 (dd, 1 H, $^3J_{5,6}$ 8.2 Hz, H-5), 3.876 (ddd, 1 H, $^3J_{6,7}$ 3.9 Hz, $^3J_{7,8a}$ 3.9 Hz, $^3J_{7,8b}$ 7.2 Hz, H-7), 3.799 (dd, 1 H, H-6), 3.637 (dd, 1 H, $^2J_{8a,8b}$ -12.0 Hz, H-8a), 3.538 (dd, 1 H, H-8b), 2.965 (dd, 1 H, $^2J_{2a,2b}$ -19.2 Hz, H-2a), 2.647 (dd, 1 H, H-2b); ^{13}C NMR (125.8 MHz, D_2O) δ 179.62 (C-1), 85.05 (C-4), 80.80 (C-3), 77.02 (C-6), 71.42 (C-5), 71.17 (C-7), 62.30 (C-8), 37.05 (C-2); MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.67; H, 5.69.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-D-*gluco*-octono-1,4-lactone (14a). Standard acetylation of **14** gave **14a** as a syrup: $[\alpha]_D^{20}$ -31.5° (*c* 0.7, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.35; ^1H NMR (500.1 MHz, $CDCl_3$) δ 5.198 (ddd, 1 H, $^3J_{6,7}$ 5.7 Hz, $^3J_{7,8a}$ 3.8 Hz, $^3J_{7,8b}$ 6.4 Hz, H-7), 5.159 (dd, 1 H, $^3J_{3,4}$ 4.5 Hz, $^3J_{4,5}$ 5.1 Hz, H-4), 5.101 (dd, 1 H, $^3J_{5,6}$ 7.7 Hz, H-5), 4.839 (ddd, 1 H, $^3J_{2a,3}$ 6.4 Hz, $^3J_{2b,3}$ 1.3 Hz, H-3), 4.330 (dd, 1 H, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 4.138 (dd, 1 H, H-6), 4.038 (dd, 1 H, H-8b), 2.771 (dd, 1 H, $^2J_{2a,2b}$ -19.1 Hz, H-2a), 2.660 (dd, 1 H, H-2b), 2.096 (s, 3 H, CH_3), 2.040 (s, 3 H, CH_3), 2.017 (s, 3 H, CH_3); ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.42 (C-1), 170.37, 169.78, 169.75 (3 × CH_3CO_2), 80.36 (C-4), 77.55 (C-3), 77.00 (C-6), 73.59 (C-5), 70.14 (C-7), 61.87 (C-8), 36.34 (C-2), 20.68, 20.55, 20.34, (3 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 331 (10) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.93; H, 5.55.

Reaction of D-Glucose and D-Mannose with Meldrum's Acid). Anhydrous D-glucose gave 1.84 g (41 %) 3,6-anhydro-2-deoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (**2**) as the only product [Lit.:[3a] 40 %], when treated according to general procedure 1. When general procedure 2 was employed, 4.14 g (91 %) of **2** were obtained from D-glucose. D-Mannose yielded 1.84 g (41 %) **2** [Lit.:[3b] 39 %], 0.18 g (4 %) 3,6-anhydro-2-deoxy-D-

glycero-D-*galacto*-octono-1,4-lactone (**15**),[6] 0.54 g (12 %) 3,7-anhydro-2-deoxy-D-*glycero*-D-*manno*-octono-1,4-lactone (**16**),[6] and 0.184 g (4 %) 2,3-dideoxy-D-*gluco*-oct-2-enono-1,4-lactone (**3**) when general procedure 1 was applied and 1.61 g (36 %) **2**, 0.23 g (5 %) **15**, 0.68 g (15 %) **16**, and 0.182 g (4 %) **3** after treatment with Meldrum's acid following general procedure 2.

3,6-Anhydro-2-deoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (2).[3a] **2** was isolated as colourless crystals: mp 115-116 °C (ethanol) [Lit.:[3a] 113-114 °C (ethanol)]; $[\alpha]_D^{20}$ +33.6° (*c* 0.5, water) [Lit.:[3a] +29° (*c* 0.5, water)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.68; ^{1}H NMR (500.1 MHz, D_2O) δ 4.958 (d, 1 H, $^3J_{3,4}$ 4.7 Hz, $^3J_{4,5}$ 0 Hz, H-4), 4.934 (dd, 1 H, $^3J_{2a,3}$ 6.2 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.405 (d, 1 H, $^3J_{5,6}$ 2.6 Hz, H-5), 3.815 (dd, 1 H, $^3J_{6,7}$ 8.8 Hz, H-6), 3.775 (ddd, 1 H, $^3J_{7,8a}$ 2.6 Hz, $^3J_{7,8b}$ 5.5 Hz, H-7), 3.665 (dd, 1 H, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 3.503 (dd, 1 H, H-8b), 2.884 (dd, 1 H, $^2J_{2a,2b}$ -19.3 Hz, H-2a), 2.587 (d, 1 H, H-2b); ^{13}C NMR (125.8 MHz, D_2O) δ 179.74 (C-1), 88.41 (C-4), 79.84 (C-3), 77.45 (C-6), 73.05 (C-5), 68.78 (C-7), 63.67 (C-8), 35.84 (C-2) [Lit.:[3a] (20.15 MHz, DMSO-d_6) δ 177.1 (C-1), 88.1 (C-4)*, 80.8 (C-6)*, 77.1 (C-3)*, 73.1 (C-5)*, 69.1 (C-7), 63.9 (C-8), 36.1 (C-2), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.77; H, 5.92.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (2a).[3a] Standard acetylation of **2** afforded **2a** as colourless crystals: mp 113-116 °C (ethanol) [Lit.:[3a] 112-113 °C (ethanol)]; $[\alpha]_D^{20}$ +72.3° (*c* 0.5, chloroform) [Lit.:[3a] +75° (*c* 0.5, chloroform)]; TLC (methyl *tert*-butyl ether) R_f 0.45; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.595 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.2 Hz, H-5), 5.184 (ddd, 1 H, $^3J_{6,7}$ 9.3 Hz, $^3J_{7,8a}$ 2.4 Hz, $^3J_{7,8b}$ 5.2 Hz, H-7), 4.984 (ddd, 1 H, $^3J_{2a,3}$ 5.4 Hz, $^3J_{2b,3}$ 1.4 Hz, $^3J_{3,4}$ 4.3 Hz, H-3), 4.842 (d, 1 H, H-4), 4.562 (dd, 1 H, $^2J_{8a,8b}$ -12.3 Hz, H-8a), 4.282 (dd, 1 H, H-6), 4.062 (dd, 1 H, H-8b), 2.784 (dd, 1 H, $^2J_{2a,2b}$ -18.8 Hz, H-2a), 2.697 (dd, 1 H, H-2b), 2.088 (s, 3 H, CH_3), 2.068 (s, 3 H, CH_3), 2.009 (s, 3 H, CH_3) [Lit.:[3a] (200 MHz, $CDCl_3$) δ 5.60 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.2 Hz, H-5), 5.18 (ddd, 1 H, $^3J_{6,7}$ 9.4 Hz, $^3J_{7,8a}$ 2.4 Hz, $^3J_{7,8b}$ 5.1 Hz, H-7), 4.99 (td, 1 H, $^3J_{2a,3}$ 5.1 Hz, $^3J_{2b,3}$ 2.2 Hz, $^3J_{3,4}$ 4.6 Hz, H-3), 4.84 (d, 1 H, H-4), .56 (dd, 1 H, $^2J_{8a,8b}$ -12.2 Hz, H-8a), 4.28 (dd, 1 H, H-6), 4.06 (dd, 1 H, H-8b), 2.78 (dd, $^2J_{2a,2b}$ -18.6 Hz, H-2a), 2.67 (dd, 1 H, H-2b), 2.09 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3)]; ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.31 (C-1), 170.60, 169.67, 169.15 (3 ×

CH_3CO_2), 85.16 (C-4), 77.70 (C-3), 77.41 (C-6), 73.67 (C-5), 67.49 (C-7), 63.05 (C-8), 35.77 (C-2), 2 × 20.70, 20.57 (3 × CH_3) [Lit.:[3a] (20.15 MHz, $CDCl_3$) δ 174.0 (C-1), 170.4, 169.5, 169.0 (3 × CH_3CO_2), 85.1 (C-4)*, 77.6 (C-3)*, 77.6 (C-5)*, 73.9 (C-6)*, 67.7 (C-7), 63.1 (C-8), 35.7 (C-2), 3 × 20.5 (3 × CH_3), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 331 (100) [MH^+], 271 (52) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.41; H, 5.21.

2,3-Dideoxy-D-*gluco*-oct-2-enono-1,4-lactone (3).[3a] **3** was obtained as colourless crystals: mp 144-148 °C (ethanol) [Lit.:[3a] 143-145 °C (ethanol)]; $[\alpha]_D^{20}$ -124.9° (*c* 0.9, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.59; ^{1}H NMR (500.1 MHz, D_2O) δ 7.907 (dd, 1 H, $^3J_{2,3}$ 5.7 Hz, $^3J_{3,4}$ 1.6 Hz, H-3), 6.261 (d, 1 H, H-2), 5.319 (dd, 1 H, $^3J_{4,5}$ 6.4 Hz, H-4), 4.072 (dd, 1 H, $^3J_{5,6}$ 1.3 Hz, H-5), 3.863 (dd, 1 H, $^3J_{7,8a}$ 2.5 Hz, $^2J_{8a,8b}$ -11.8 Hz, H-8a), 3.751 (ddd, 1 H, $^3J_{6,7}$ 8.9 Hz, $^3J_{7,8b}$ 4.4 Hz, H-7), 3.725 (dd, 1 H, H-6), 3.659 (dd, 1 H, H-8b) [Lit.:[3a] (80.1 MHz, DMSO-d_6): δ 7.83 (dd, 1 H, $^3J_{2,3}$ 5.7 Hz, $^3J_{3,4}$ 1.5 Hz, H-3), 6.19 (dd, 1 H, $^4J_{2,4}$ 1.9 Hz, H-2), 5.09 (dt, 1 H, $^3J_{4,5}$ 6.8 Hz, H-4),4.20 – 3.00 (m, H-5, H-6, H-7, H-8a, and H-8b); ^{13}C NMR (125.8 MHz, D_2O) δ 176.74 (C-1), 158.15 (C-3), 121.63 (C-2), 85.50 (C-4), 71.04 (C-5), 70.70 (C-6), 70.36 (C-7), 63.36 (C-8); MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+], 187 (20) [MH^+ -H_2O].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 47.30; H, 5.90.

3,6-Anhydro-2-deoxy-D-*glycero*-D-*galacto*-octono-1,4-lactone (15).[6] **15** was obtained as colourless crystals: mp 159-162 °C (ethanol); $[\alpha]_D^{20}$ -59.6° (*c* 0.5, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.52; ^{1}H NMR (300.1 MHz, D_2O) δ 5.127 (dd, 1 H, $^3J_{3,4}$ 6.5 Hz, $^3J_{4,5}$ 5.4 Hz, H-4), 4.665 (ddd, 1 H, $^3J_{2a,3}$ 7.7 Hz, $^3J_{2b,3}$ 2.4 Hz, H-3), 4.474 (dd, 1 H, $^3J_{5,6}$ 3.6 Hz, H-5), 3.866 (ddd, 1 H, $^3J_{6,7}$ 8.7 Hz, $^3J_{7,8a}$ 2.9 Hz, $^3J_{7,8b}$ 5.7 Hz, H-7), 3.708 (dd, 1 H, H-6), 3.688 (dd, 1 H, $^2J_{8a,8b}$ -12.2 Hz, H-8a), 3.534 (dd, 1 H, H-8b), 2.891 (dd, 1 H, $^2J_{2a,2b}$ -19.2 Hz, H-2a), 2.592 (dd, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.81 (C-1), 84.06 (C-4), 81.38 (C-3), 76.60 (C-6), 70.18 (C-5), 68.88 (C-7), 63.42 (C-8), 35.58 (C-2); MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.25; H, 5.12.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-D-*galacto*-octono-1,4-lactone (15a). Acetylation of **15** yielded **15a** as a syrup: $[\alpha]_D^{20}$ -52.9° (*c* 0.4, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.31; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.479 (dd, 1 H, $^3J_{4,5}$ 5.5 Hz, $^3J_{5,6}$ 3.9 Hz, H-5), 5.323 (ddd, 1 H, $^3J_{6,7}$ 8.8 Hz, $^3J_{7,8a}$ 2.5 Hz, $^3J_{7,8b}$ 5.2 Hz,

H-7), 5.112 (dd, 1 H, $^3J_{3,4}$ 6.6 Hz, H-4), 4.732 (ddd, 1 H, $^3J_{2a,3}$ 7.5 Hz, $^3J_{2b,3}$ 2.9 Hz, H-3), 4.553 (dd, 1 H, $^2J_{8a\,8b}$ -12.2 Hz, H-8a), 4.121 (dd, 1 H, H-8b), 4.089 (dd, 1 H, H-6), 2.797 (dd, 1 H, $^2J_{2a\,2b}$ -18.9 Hz, H-2a), 2.700 (dd, 1 H, H-2b), 2.095 (s, 3 H, CH_3), 2.067 (s, 3 H, CH_3), 2.018 (s, 3 H, CH_3); ^{13}C NMR (75.8 MHz, D_2O) δ 174.14 (C-1), 170.49 169.56, 169.43 (3 × CH_3CO_2), 80.52 (C-4), 78.58 (C-3), 76.66 (C-6), 70.68 (C-5), 68.05 (C-7), 62.85 (C-8), 35.30 (C-2), 2 × 20.68, 20.26 (3 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 331 (2) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.36; H, 5.60.

3,7-Anhydro-2-deoxy-D-*glycero*-D-*galacto*-octono-1,4-lactone (16).[6] **16** was obtained as colourless crystals: mp 131-133 °C (ethanol) [Lit.:[3b,6] 166-167 °C (ethanol)]; $[\alpha]_D^{20}$ -104.8° (*c* 0.6, water) [Lit.:[3b,6] +136° (*c* 1, chloroform)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.48; ^{1}H NMR (300.1 MHz, D_2O) δ 4.743 (dd, 1 H, $^3J_{3,4}$ 1.9 Hz, $^3J_{4,5}$ 4.0 Hz, H-4), 4.484 (dd, 1 H, $^3J_{2a,3}$ 4.1 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 3.849 (dd, 1 H, $^3J_{5,6}$ 9.6 Hz, H-5), 3.516 (dd, 1 H, $^3J_{6,7}$ 9.7 Hz, H-6), 3.785 (dd, 1 H, $^3J_{7,8a}$ 2.2 Hz, $^2J_{8a\,8b}$ -12.3 Hz, H-8a), 3.593 (dd, 1 H, $^3J_{7,8b}$ 6.2 Hz, H-8b), 3.341 (ddd, 1 H, H-7), 2.913 (dd, 1 H, $^2J_{2a\,2b}$ -17.7 Hz, H-2a), 2.526 (d, 1 H, H-2b) [Lit.:[3b,6] (200 MHz, DMSO-d_6) 5.29 (d, 1 H, $^3J_{5,OH}$ 5.7 Hz, OH-5), 5.02 (d, 1 H, $^3J_{7,OH}$ 5.2 Hz, OH-7), 4.52 (t, 1 H, $^3J_{8\,OH}$ 5.6 Hz, OH-8), 4.52 (dd, 1 H, $^3J_{3,4}$ 1.9 Hz, $^3J_{4,5}$ 4.0 Hz, H-4), 4.31 (dd, 1 H, $^3J_{2a,3}$ 4.0 Hz, $^3J_{2b\,3}$ 0 Hz, H-3), 3.70 – 3.10 (m, 5 H, H-5, H-6, H-7, H-8a, and H-8b), 2.87 (dd, 1 H, $^2J_{2a\,2b}$ – 16.9 Hz, H-2a), 2.28 (d, 1 H, H-2b)]; ^{13}C NMR (75.8 MHz, D_2O) δ 179.26 (C-1), 38.18 (C-2), 73.84 (C-3), 82.75 (C-4), 71.48 (C-5), 66.90 (C-6), 78.38 (C-7), 60.99 (C-8) [Lit.:[3b,6] (20.15 MHz, DMSO-d_6) 175.6 (C-1), 81.6, 79.4, 72.9, 71.6, 66.8 (C-3, c-4, C-5, C-6, and C-7), 61.0 (C-8), 37.8 (C-2)]; MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+]. HRMS (CI, *iso*-butane) Calcd for $C_8H_{13}O_6^+$: 205.0712. Found: 205.0655.

5,6,8-Tri-*O*-acetyl-3,7-anhydro-2-deoxy-D-*glycero*-D-*manno*-octono-1,4-lactone (16a). Standard acetylation of **16** returned **16a** as colourless crystals: mp 156-158 °C; $[\alpha]_D^{20}$ -139.0° (*c* 0.5, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.36; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.193 (dd, 1 H, $^3J_{5,6}$ 9.8 Hz, $^3J_{6,7}$ 9.7 Hz, H-6), 5.080 (dd, 1 H, $^3J_{4,5}$ 3.8 Hz, H-5), 4.691 (dd, 1 H, $^3J_{3,4}$ 1.9 Hz, H-4), 4.406 (ddd, 1 H, $^3J_{2a,3}$ 3.8 Hz, $^3J_{2b,3}$ 1.1 Hz, H-3), 4.111 (dd, 1 H, $^3J_{7,8a}$ 5.1 Hz, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 4.059 (dd, 1 H, $^3J_{7,8b}$ 2.5 Hz, H-8b), 3.626 (ddd, 1 H, H-7), 2.654 (dd, 1 H, $^2J_{2a\,2b}$ -17.5 Hz, H-2a), 2.594 (dd, 1 H, H-2b), 2.038 (s, 3 H, CH_3), 2.001 (s, 3 H, CH_3), 1.982 (s, 3 H, CH_3); ^{13}C NMR

(75.8 MHz, $CDCl_3$) δ 173.60 (C-1), 170.53, 170.37, 169.18 (3 × CH_3CO_2), 77.75 (C-4), 74.95 (C-3), 73.54 (C-7), 71.04 (C-5), 65.35 (C-6), 62.19 (C-8), 37.53 (C-2), 20.60, 20.55, 20.48 (3 × CH_3). MS (CI, *iso*-butane): *m/z* (%) 331 (100) [MH^+], 271 (16) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.90; H, 6.00.

Reaction of D-Galactose and D-Talose with Meldrum's Acid). D-Galactose afforded 2.72 g (60 %) 3,6-anhydro-2-deoxy-D-*glycero*-L-*gluco*-octono-1,4-lactone (**17**) and 0.69 g (15 %) 3,6-anhydro-2-deoxy-D-*glycero*-L-*altro*-octono-1,4-lactone (**18**) [Lit.[3a] 45 % and 7 %, respectively] when treated in accordance with general procedure 1. When general procedure 2 was employed 2.54 g (56 %) **17**, and 1.38 g (30 %) **18** were obtained. 1.33 g (29 %) **17** and 1.34 g (30 %) **18** were generated from D-talose when general procedure 1 was utilised and 0.99 g (22 %) **17** and 2.99 g (67 %) **18** after treatment with Meldrum's acid following general procedure 2.

3,6-Anhydro-2-deoxy-D-*glycero*-L-*gluco*-octono-1,4-lactone (17).[3a] **17** was isolated as colourless crystals: mp 97-98 °C (ethanol) [Lit.:[3a] 93-94 °C (ethanol)]; $[\alpha]_D^{20}$ +26.2° (*c* 1.1, water) [Lit.:[3a] +27° (*c* 1.0, water)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.62; ^{1}H NMR (300.1 MHz, D_2O) δ 5.008 (dd, 1 H, $^3J_{3,4}$ 4.3 Hz, $^3J_{4,5}$ 1.3 Hz, H-4), 4.920 (dd, 1 H, $^3J_{2a,3}$ 5.9 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.389 (dd, 1 H, $^3J_{5,6}$ 5.7 Hz, H-5), 3.853 (dd, 1 H, $^3J_{6,7}$ 4.2 Hz, H-6), 3.781 (ddd, 1 H, $^3J_{7,8a}$ 4.5 Hz, $^3J_{7,8b}$ 7.0 Hz, H-7), 3.661 (dd, 1 H, $^2J_{8a,8b}$ -11.9 Hz, H-8a), 3.603 (dd, 1 H, H-8b), 2.962 (dd, 1 H, $^2J_{2a,2b}$ -19.1 Hz, H-2a), 2.719 (d, 1 H, H-2b) [Lit.:[3a] (200 MHz, DMSO-d_6) 4.76 (d, 1 H, OH-7), 4.71 (d, 1 H, $^3J_{4,5}$ 0 Hz, H-4), 4.66 (t, 1 H, OH-8), 4.59 (t, 1 H, $^3J_{2a,3}$ 5.9 Hz, $^3J_{2b,3}$ 0 Hz, $^3J_{3,4}$ 5.9 Hz, H-3), 4.58 (d, 1 H, OH-5), 4.16 (t, 1 H, $^3J_{5,6}$ 6.0 Hz, H-5), 3.65 (dd, 1 H, $^3J_{6,7}$ 3.2 Hz, H-6), 3.47 (m, 1 H, H-7), 3.39 (m, 2 H, H-8a and H-8b), δ 2.80 (dd, 1 H, $^2J_{2a,2b}$ –18.2 Hz, H-2a), 2.45 (d, 1 H, H-2b)]; ^{13}C NMR (75.8 MHz, D_2O) δ 179.37 (C-1), 91.22 (C-4), 85.94 (C-3), 78.11 (C-6), 76.19 (C-5), 71.01 (C-7), 63.10 (C-8), 36.09 (C-2) [Lit.:[3a] (20.15 MHz, DMSO-d_6) δ 175.8 (C-1), 90.6 (C-4)*, 85.8 (C-6)*, 76.8 (C-3)*, 75.5 (C-5)*, 70.1 (C-7), 62.8 (C-8), 35.7 (C-2), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+]. HRMS (CI, *iso*-butane) Calcd for $C_8H_{13}O_6^+$: 205.0712. Found: 205.0640.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-L-*gluco*-octono-1,4-lactone (17a).[3a] Acetylation of **17** returned **17a** as a syrup: $[\alpha]_D^{20}$+64.3° (*c* 0.8, chloroform)

[Lit.:[3a] mp 66-67 °C (ethanol), $[\alpha]_D^{20}$ +77° (*c* 1.0, chloroform)]; TLC (methyl *tert*-butyl ether) R_f 0.44; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.375 (ddd, 1 H, $^3J_{6,7}$ 2.9 Hz, $^3J_{7,8a}$ 7.0 Hz, $^3J_{7,8b}$ 5.1 Hz, H-7), 5.162 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.7 Hz, H-5), 4.882 (dd, 1 H, $^3J_{2a,3}$ 2.8 Hz, $^3J_{2b,3}$ 0 Hz, $^3J_{3,4}$ 4.3 Hz, H-3), 4.857 (d, 1 H, H-4), 4.258 (dd, 1 H, $^2J_{8a,8b}$ -11.6 Hz, H-8a), 4.181 (dd, 1 H, H-6), 4.152 (dd, 1 H, H-8b), 2.703 (dd, 1 H, $^2J_{2a,2b}$ -18.6 Hz, H-2a), 2.769 (d, 1 H, H-2b), 2.112 (s, 6 H, 2 × CH_3), 2.040 (s, 3 H, CH_3) [Lit.:[3a] (200 MHz, $CDCl_3$): δ 5.36 (ddd, 1 H, $^3J_{6,7}$ 3.5 Hz, $^3J_{7,8a}$ 4.9 Hz, $^3J_{7,8b}$ 7.0 Hz, H-7), 5.15 (d, 1 H, $^3J_{4,5}$ 0 Hz, $^3J_{5,6}$ 3.5 Hz, H-5), 4.92 (s, 1 H, $^3J_{2b,3}$ 0 Hz, H-3), 4.92 (s, 1 H, H-4), 4.24 (dd, 1 H, $^2J_{8a,8b}$ -11.6 Hz, H-8a), 4.20 (t, 1 H, H-6), 4.16 (dd, 1 H, H-8b), 2.80 (m, 1 H, $^2J_{2a,2b}$ -18.5 Hz, H-2a), 2.73 (d, 1 H, H-2b), 2.13 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3)]; ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 173.95 (C-1), 2 × 170.39, 169.47 (3 × CH_3CO_2), 86.59 (C-4), 84.30 (C-6), 78.51 (C-5), 78.00 (C-3), 69.44 (C-7), 62.53 (C-8), 36.02 (C-2), 3 × 20.55 (3 × CH_3) [Lit.:[3a] (20.15 MHz, $CDCl_3$) δ 174.1 (C-1), 170.1, 169.3 (3 × CH_3CO_2), 86.3 (C-4)*, 83.7 (C-6)*, 78.2 (C-5)*, 77.5 (C-3)*, 69.1 (C-7), 62.2 (C-8), 35.7 (C-2), 3 × 20.2 (3 × CH_3), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 331 (7) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.30; H, 4.87.

3,6-Anhydro-2-deoxy-D-*glycero*-L-*altro*-octono-1,4-lactone (18).[3a] **18** was obtained as colourless crystals: mp 127-130 °C (ethanol) [Lit.:[3a] 129 °C (ethanol)]; $[\alpha]_D^{20}$ -121.6° (*c* 1.1, water) [Lit.:[3a] -122° (*c* 0.5, water)]; TLC (methyl *tert*-butyl ether) R_f 0.46; ^{1}H NMR (300.1 MHz, D_2O) δ 5.048 (dd, 1 H, $^3J_{3,4}$ 4.6 Hz, $^3J_{4,5}$ 4.6 Hz, H-4), 4.841 (dd, 1 H, $^3J_{2a,3}$ 6.4 Hz, $^3J_{2b,3}$ 0 Hz, H-3), 4.304 (dd, 1 H, $^3J_{5,6}$ 8.6 Hz, H-5), 3.740 (dd, 1 H, $^3J_{6,7}$ 2.6 Hz, H-6), 3.703 (ddd, 1 H, $^3J_{7,8a}$ 4.8 Hz, $^3J_{7,8b}$ 7.5 Hz, H-7), 3.589 (dd, 1 H, $^2J_{8a,8b}$ -11.5 Hz, H-8a), 3.534 (dd, 1 H, H-8b), 2.949 (dd, 1 H, $^2J_{2a,2b}$ -19.1 Hz, H-2a), 2.629 (d, 1 H, H-2b) [Lit.:[3a] (200 MHz, DMSO-d_6) δ 5.37 (d, 1 H, OH-5), 4.88 (t, 1 H, $^3J_{3,4}$ 4.6 Hz, $^3J_{4,5}$ 4.6 Hz, H-4), 4.67 (t, 1 H, $^3J_{2a,3}$ 5.8 Hz, $^3J_{2b,3}$ 1.4 Hz, H-3), 4.61 (d, 1 H, OH-7), 4.60 (t, 1 H, OH-8), 4.20 (ddd, 1 H, $^3J_{5,6}$ 8.1 Hz, H-5), 3.93 (m, H-7, H-8a, and H-8b), 3.70 (dd, 1 H, $^3J_{6,7}$ 1.6 Hz, H-6), 2.86 (dd, 1 H, $^2J_{2a,2b}$ –18.3 Hz, H-2a), 2.43 (dd, 1 H, H-2b)]; ^{13}C NMR (75.8 MHz, D_2O) δ 179.73 (C-1), 84.60 (C-4), 80.04 (C-3), 77.07 (C-6), 71.54 (C-5), 70.06 (C-7), 63.26 (C-8), 36.99 (C-2) [Lit.:[3a] (20.15 MHz, DMSO-d_6) δ 176.5 (C-1), 83.8 (C-4)*, 80.5 (C-6)*, 76.3 (C-3)*, 71.3 (C-5)*, 69.8 (C-7), 62.8 (C-8), 37.1 (C-2), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.67; H, 5.69.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-L-*altro*-octono-1,4-lactone (18a).[3a] Standard acetylation of **18** afforded **18a** as a syrup: $[\alpha]_D^{20}$ -134.6° (*c* 0.3, chloroform) [Lit.:[3a] -185° (*c* 1.0, chloroform)]; TLC (methyl *tert*-butyl ether) R_f 0.48; ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 5.173 (ddd, 1 H, $^3J_{6,7}$ 3.4 Hz, $^3J_{7,8a}$ 4.9 Hz, $^3J_{7,8b}$ 6.8 Hz, H-7), 5.145 (dd, 1 H, $^3J_{3,4}$ 4.3 Hz, $^3J_{4,5}$ 4.8 Hz, H-4), 4.912 (dd, 1 H, $^3J_{5,6}$ 8.0 Hz, H-5), 4.897 (ddd, 1 H, $^3J_{2a,3}$ 6.3 Hz, $^3J_{2b,3}$ 1.3 Hz, H-3), 4.249 (dd, 1 H, $^2J_{8a,8b}$ -11.8 Hz, H-8a), 4.191 (dd, 1 H, H-6), 4.161 (dd, 1 H, H-8b), 2.801 (dd, 1 H, $^2J_{2a,2b}$ -18.8 Hz, H-2a), 2.662 (dd, 1 H, H-2b), 2.107 (s, 3 H, CH_3), 2.094 (s, 3 H, CH_3), 2.030 (s, 3 H, CH_3) [Lit.:[3a] (200 MHz, $CDCl_3$) δ 5.21 (ddd, 1 H, $^3J_{6,7}$ 3.3 Hz, $^3J_{7,8a}$ 5.2 Hz, $^3J_{7,8b}$ 6.7 Hz, H-7), 5.17 (t, 1 H, $^3J_{3,4}$ 4.7 Hz, $^3J_{4,5}$ 4.7 Hz, H-4), 4.94 (ddd, 1 H, $^3J_{2a,3}$ 6.4 Hz, $^3J_{2b,3}$ 1.8 Hz, H-3), 4.93 (dd, 1 H, $^3J_{5,6}$ 8.1 Hz, H-5), 4.28 (dd, 1 H, $^2J_{8a,8b}$ -11.9 Hz, H-8a), 4.22 (dd, 1 H, H-6), 4.18 (dd, 1 H, H-8b), 2.83 (dd, 1 H, $^2J_{2a,2b}$ -18.9Hz, H-2a), 2.70 (dd, 1 H, H-2b), 2.14 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3)]; ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.51 (C-1), 170.35, 169.95, 169.87 (3 × CH_3CO_2), 80.16 (C-4), 77.53 (C-6), 77.07 (C-5), 72.68 (C-3), 69.18 (C-7), 62.28 (C-8), 36.31 (C-2), 20.68, 20.57, 20.32 (3 × CH_3) [Lit.:[3a] (75.8 MHz, $CDCl_3$) δ 174.3 (C-1), 170.3, 169.9 (3 × CH_3CO_2), 80.3 (C-4)*, 77.9 (C-3)*, 77.1 (C-5)*, 72.9 (C-6)*, 69.5 (C-7), 62.4 (C-8), 36.3 (C-2), 20.6, 20.5, 20.3 (3 × CH_3), *assignments may be interchanged]; MS (CI, *iso*-butane): *m/z* (%) 331 (4) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.44; H, 5.15.

Reaction of D-Idose and D-Gulose with Meldrum's Acid). D-Idose gave 2.72 g (60 %) 3,6-anhydro-2-deoxy-D-*glycero*-L-*ido*-octono-1,4-lactone (**19**) as a single product when treated in accordance with general procedure 1. When general procedure 2 was utilized 3.40 g (75 %) **19** were obtained. 3.22 g (71 %) **19** and 0.28 g (6 %) 3,6-anhydro-2-deoxy-D-*glycero*-L-*galacto*-octono-1,4-lactone (**20**) were obtained from D-gulose when general procedure 1 was applied and 1.84 g (41 %) **19** and 0.19 g (4 %) **20** after treatment with Meldrum's acid following general procedure 2.

3,6-Anhydro-2-deoxy-D-*glycero*-L-*ido*-octono-1,4-lactone (19). 19 was isolated as colourless crystals: mp 123-125 °C (ethanol); $[\alpha]_D^{20}$ -18.8° (*c* 1.1, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.53; ^{1}H NMR (300.1 MHz, D_2O) 4.939 (dd, 1 H,

$^3J_{2a\,3}$ 6.4 Hz, $^3J_{2b,3}$ 0 Hz, $^3J_{3\,4}$ 3.8 Hz, H-3), 4.933 (d, 1 H, $^3J_{4\,5}$ 0 Hz, H-4), 4.310 (d, 1 H, $^3J_{5\,6}$ 2.5 Hz, H-5), 3.805 (dd, 1 H, $^3J_{6,7}$ 7.4 Hz, H-6), 3.781 (ddd, 1 H, $^3J_{7,8a}$ 3.2 Hz, $^3J_{7,8b}$ 6.4 Hz, H-7), 3.563 (dd, 1 H, $^2J_{8a\,8b}$ -12.0 Hz, H-8), 3.454 (dd, 1 H, H-8b), δ 2.868 (dd, 1 H, $^2J_{2a\,2b}$ -19.7 Hz, H-2a), 2.557 (d, 1 H, H-2b); ^{13}C NMR (75.8 MHz, D_2O) δ 179.62 (C-1), 89.06 (C-4), 80.81 (C-3), 76.68 (C-6), 73.14 (C-5), 70.82 (C-7), 62.74 (C-8), 35.75 (C-2); MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.97; H, 6.00.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-L-*ido*-octono-1,4-lactone (19a). Standard acetylation of **19** gave **19a** as a syrup: $[\alpha]_D^{20}$ -35.1° (*c* 1.4, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.42; ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 5.364 (d, 1 H, $^3J_{4\,5}$ 1.1 Hz, $^3J_{5\,6}$ 5.0 Hz, H-5), 5.189 (ddd, 1 H, $^3J_{6\,7}$ 6.1 Hz, $^3J_{7,8a}$ 3.9 Hz, $^3J_{7,8b}$ 6.6 Hz, H-7), 4.956 (ddd, 1 H, $^3J_{2a,3}$ = 1.1 Hz, $^3J_{2b,3}$ 6.0 Hz, $^3J_{3,4}$ 5.0 Hz, H-3), 4.877 (dd, 1 H, H-4), 4.363 (dd, 1 H, H-6), 4.245 (dd, 1 H, $^2J_{8a\,8b}$ -12.1 Hz, H-8a), 3.934 (dd, 1 H, H-8b), 2.738 (dd, 1 H, $^2J_{2a,2b}$ -19.3 Hz, H-2a), 2.620 (dd, 1 H, H-2b), 2.067 (s, 3 H, CH_3), 2.047 (s, 3 H, CH_3), 1.978 (s, 3 H, CH_3); ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.51 (C-1), 170.28, 2 × 169.62 (3 × CH_3CO_2), 85.92 (C-4), 77.63 (C-3), 76.86 (C-5), 75.63 (C-6), 69.47 (C-7), 62.23 (C-8), 35.54 (C-2), 20.85, 2 × 20.43 (3 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 331 (84) [MH^+], 271 (100) [MH^+ - HOAc]; HRMS (CI, *iso*-butane): Calcd for $C_{14}H_{19}O_9^+$: 331.1029. Found: 331.1029.

3,6-Anhydro-2-deoxy-D-*glycero*-L-*galacto*-octono-1,4-lactone (20). 20 was obtained as colourless crystals: mp 143–146 °C (ethanol); $[\alpha]_D^{20}$ +44.8° (*c* 0.7, water); TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.29; ^{1}H NMR (500.1 MHz, D_2O) δ 5.120 (dd, 1 H, $^3J_{3,4}$ 6.1 Hz, $^3J_{4,5}$ 5.5 Hz, H-4), 4.669 (ddd, 1 H, $^3J_{2a,3}$ 2.2 Hz, $^3J_{2b,3}$ 7.7 Hz, H-3), 4.440 (dd, 1 H, $^3J_{5,6}$ 4.4 Hz, H-5), 3.872 (ddd, 1 H, $^3J_{6\,7}$ 6.6 Hz, $^3J_{7,8a}$ 3.9 Hz, $^3J_{7,8b}$ 6.6 Hz, H-7), 3.787 (dd, 1 H, H-6), 3.666 (dd, 1 H, $^2J_{8a,8b}$ -12.1 Hz, H-8a), 3.542 (dd, 1 H, H-8b), 2.919 (dd, 1 H, $^2J_{2a\,2b}$ -19.2 Hz, H-2a), 2.648 (dd, 1 H, H-2b); ^{13}C NMR (125.8 MHz, D_2O) δ 179.90 (C-1), 84.30 (C-4), 82.26 (C-3), 76.19 (C-6), 70.40 (C-5), 70.40 (C-7), 62.81 (C-8), 35.84 (C-2); MS (CI, *iso*-butane): *m/z* (%) 205 (100) [MH^+], 187 (54) [MH^+- H_2O], 169 (55) [MH^+- $2H_2O$].

Anal. Calcd for $C_8H_{12}O_6$ (204.18): C, 47.06; H, 5.92. Found: C, 46.63; H, 5.27.

5,7,8-Tri-*O*-acetyl-3,6-anhydro-2-deoxy-D-*glycero*-L-*galacto*-octono-1,4-lactone (20a). Standard acetylation of **20** afforded **20a** as colourless crystals: mp 129-

132 °C; $[\alpha]_D^{20}$ +69.1° (*c* 0.6, chloroform); TLC (methyl *tert*-butyl ether) R_f 0.29; ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 5.413 (dd, 1 H, $^3J_{4,5}$ 5.7 Hz, $^3J_{5,6}$ 7.0 Hz, H-5), 5.248 (ddd, 1 H, $^3J_{6,7}$ 3.8 Hz, $^3J_{7,8a}$ 4.5 Hz, $^3J_{7,8b}$ 7.0 Hz, H-7), 5.068 (dd, 1 H, $^3J_{3,4}$ 5.1 Hz, H-4), 4.725 (ddd, 1 H, $^3J_{2a,3}$ 5.1 Hz, $^3J_{2b,3}$ 3.2 Hz, H-3), 4.330 (dd, 1 H, H-6), 4.309 (dd, 1 H, $^2J_{8a,8b}$ -11.4 Hz, H-8a), 4.037 (dd, 1 H, H-8b), 2.744 (dd, 1 H, $^2J_{2a,2b}$ -22.8 Hz, H-2a), 2.739 (dd, 1 H, H-2b), 2.100 (s, 3 H, CH_3), 2.098 (s, 3 H, CH_3), 2.023 (s, 3 H, CH_3); ^{13}C NMR (75.8 MHz, $CDCl_3$) δ 174.45 (C-1), 170.44, 170.24, 169.93 (3 × CH_3CO_2), 80.61 (C-4), 78.43 (C-3), 76.59 (C-6), 72.31 (C-5), 68.23 (C-7), 62.74 (C-8), 36.30 (C-2), 20.73, 20.61, 20.26 (3 × CH_3); MS (CI, *iso*-butane): *m/z* (%) 331 (26) [MH^+], 271 (100) [MH^+ - HOAc].

Anal. Calcd for $C_{14}H_{18}O_9$ (330.29): C, 50.91; H, 5.49. Found: C, 50.68; H, 5.27.

Reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (29) with 1.[3b] 0.91 g (2.6 mmol) of **29** were dissolved in 2 mL of acetonitrile and 0.74 g (5.18 mmol) of **1** and 0.36 mL (2.6 mmol) of triethylamine were added. The resulting mixture was heated to 40 °C for two days. The solvent was evaporated *in vacuo*. Column chromatography on silica gel with chloroform/methanol 20/1 (v/v) as the eluent gave 0.72 g (59 %) [Lit.:[3b] 59 %] 2,2-dimethyl-5-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-1,3-dioxan-4,6-dione (**30**): mp 132-134 °C [Lit.:[3b] 192-194 °C (90 % aq ethanol)]; $[\alpha]_D^{20}$ -7.6° (*c* 1.0, chloroform) [Lit.:[3b] +12° (*c* 1.0, ethanol)]; TLC (ethyl acetate/ethanol/water 14/4/1 v/v/v) R_f 0.53; ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 5.729 (dd, 1 H, $^3J_{1',2'}$ 10.2 Hz, $^3J_{2',3'}$ 9.5 Hz, H-2'), 5.156 (dd, 1 H, $^3J_{3',4'}$ 9.5 Hz, H-3'), 5.045 (dd, 1 H, $^3J_{4',5'}$ 10.2 Hz, H-4'), 4.383 (dd, 1 H, $^3J_{1',5'}$ 1.6 Hz, H-1'), 4.096 (dd, 1 H, $^2J_{6a',6b'}$ -12.1 Hz, $^3J_{5',6a'}$ 2.5 Hz, H-6a'), 4.041 (dd, 1 H, $^3J_{5',6b'}$ 5.1 Hz, H-6b'), 3.674 (ddd, 1 H, H-5'), 3.577 (d, 1 H, H-5), 1.988 (s, 3 H, CO_2CH_3), 1.977 (s, 6 H, 2 × CO_2CH_3), 1.960 (s, 3 H, CO_2CH_3), 1.722 (s, 3 H, CH_3), 1.692 (s, 3 H, CH_3) [Lit.:[3b] (200 MHz, DMSO-d_6) δ 5.74 (t, 1 H, $^3J_{1',2'}$ 10.0 Hz, $^3J_{2',3'}$ 9.5 Hz, H-2'), 5.04 (t, 1 H, $^3J_{3',4'}$ 9.5 Hz, H-3'), 4.84 (t, 1 H, $^3J_{4',5'}$ 9.5 Hz, H-4'), 4.42 (d, 1 H, $^3J_{1',5'}$ 0 Hz, H-1'), 4.10 (dd, 1 H, $^3J_{5',6a'}$ 5.0 Hz, $^2J_{6a',6b'}$ –11.8 Hz, H-6a'), 3.87 (dd, 1 H, $^3J_{5',6b'}$ 2.5 Hz, H-6b'), 3.75-3.50 (m, 1 H, H-5'), 1.99, 1.96, 1.88, 1.79 (4s, 12 H, 4 × CO_2CH_3), 1.38 (s, 6 H, 2 × CH_3)]; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.22, 169.40, 169.19 (4 × $CH_3\underline{C}O_2$), 164.35, 161.75 (C-4, C-6), 106.02 (C-2), 76.14 (C-5'), 75.88 (C-2'), 74.16 (C-1'), 69.52 (C-4'), 67.80 (C-3'), 61.63 (C-6'), 45.83 (C-5), 28.42, 27.78

(CH_3), 20.58, 2 × 20.48, 20.41 (4 × $CO_2\underline{C}H_3$) [Lit.:[3b] (20.15 MHz, DMSO-d_6) δ 169.8 169.4, 169.0, 168.2 (4 × $CH_3\underline{C}O_2$), 146.7 (C-4, C-6), 98.9 (C-2), 75.3, 75.0, 73.8, 69.3, 68.9 (C-1', C-2', C-3', C-4', and C-5'), 62.7 (C-6'), 70.3 (C-5), 25.5 (CH_3), 20.1 (4 × $CO_2\underline{C}H_3$)]; MS (CI, *iso*-butane): *m/z* (%) 313 (100) [MH^+ -H_2O –$C_6H_7O_4$].

Anal. Calcd for $C_{20}H_{26}O_{13}$ (474.42): C, 50.63; H, 5.52. Found: C, 50.56; H, 5.53.

30 was subsequently deacetylated. Therefore, 0.72 g (1.5 mmol) of **30** were dissolved in 20 mL of abs methanol and cooled to 0 °C. A solution of 0.21 g (9.0 mmol) sodium in 10 ml of abs methanol was added dropwise upon cooling to 0 °C. After one hour tlc monitoring revealed the reaction to be completed. The mixture was neutralized by adding ion exchange resin Amberlite™ IR 120/H^+. After filtration from the resin, the solvent was removed *in vacuo*. NMR spectra were taken from the raw material and the compound **25** was used in the next step without any further purification: ^{1}H NMR (500.1 MHz, D_2O): δ 4.017 (d, 1 H, $^3J_{1',2'}$ 10.2 Hz, $^3J_{1',5'}$ 0 Hz, H-1'), 3.901 (dd, 1 H, $^3J_{3',4'}$ 9.5 Hz, $^3J_{4',5'}$ 9.5 Hz, H-4'), 3.619 (dd, 1 H, $^3J_{5',6a'}$ 1.9 Hz, $^2J_{6a',6b'}$ -12.1 Hz, H-6a'), 3.543 (dd, 1 H, $^3J_{5',6b'}$ 4.5 Hz, H-6b'), 3.294 (dd, 1 H, $^3J_{2',3'}$ 8.9 Hz, H-3'), 3.233 (dd, 1 H, H-2'), 3.187 (ddd, 1 H, H-5'), 2.000 (s, 1 H, H-5), 1.425 (s, 6 H, 2 × CH_3); ^{13}C NMR (125.8 MHz, D_2O) δ 169.35 (C-4, C-6), 103.44 (C-2), 79.68 (C-5'), 78.62 (C-2'), 76.18 (C-1'), 74.91 (C-5), 70.07 (C-4'), 69.76 (C-3'), 61.02 (C-6'), 24.81 (2 × CH_3). **25** was dissolved in DMF and triethylamine was added. The resulting mixture was heated to 40 °C for 5 days to give **2** (see above) in almost quantitative yields.

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6. The structure of the major by-product of the reaction of D-mannose with Meldrum's acid was originally proposed to be that of compound **15**, see reference 3b. However, we were able correct this erroneous previous structural assignment and prove that compound **16** is the major by-product of this reaction whereas **15** is only formed to a very small extent.