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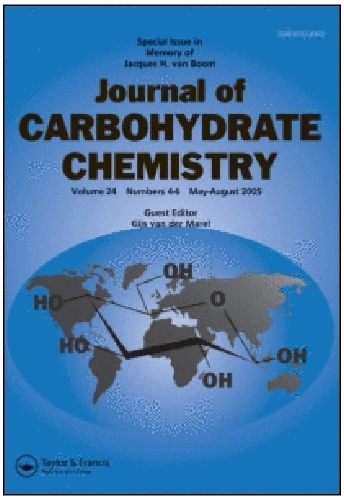

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Some Novel Types of Nitrosugars

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SOME NOVEL TYPES OF NITROSUGARS[1]

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ABSTRACT

The stereochemistry of the reaction of the conjugate base of nitromethane with aldehydosugars was shown to depend on the reaction conditions and the structure of the glycosyl group. Some reactions of a novel type of synthetic intermediates in carbohydrate chemistry, the gem-bromonitroenoses are described.

INTRODUCTION

Nitrosugars constitute useful synthetic intermediates.[3] To still increase their potentialities, we applied to nitrosugars our strategy[4] of building reactive polyfunctional substructures. So, we describe here the synthesis of nitrosugars bearing in the vicinity of their nitro group other reactive moieties like halogens, double bonds, keto or dialkylphosphono groups, aziridine or oxirane. The focus of this paper will be on the stereochemical aspects of the synthesis of these compounds. Some synthetic applications of these novel nitrosugars will be reported in a future publication. A preliminary account of part of this work has been published.[5]

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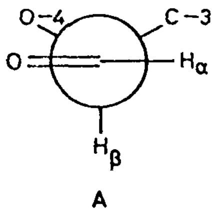
RESULTS AND DISCUSSION

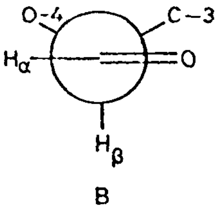
The aldehydosugars **1**^{6,7,8}, **2**^{9,10} and **3**^{11,7} were known[12] whereas **4** was prepared from **18**[13] following the sequence shown in Scheme 1.

Addition of the anion of nitromethane on these aldehydes (Henry's reaction) using the mild conditions described by Szarek[14] ($MeNO_2$, MeOH, MeONa, 2.5 h, 0° C) gave exclusively one isomer of the expected nitroalcohol when no oxygen was present at C-3 on the α face of the aldehydosugar (**1** and **2**). The isomerically pure nitroalcohols **9** and **10** were shown to belong to the D series from their negative Cotton effect.[15] Compounds **5** and **6** were obtained as epimeric mixtures (as much as 50% of the L-*talo* isomer for **5**, 14% for **6**). When the reactions conditions were made more severe, following Baer's procedure,[16] the stereospecificity observed for **1** and **2** in the previous mild conditions was lost.

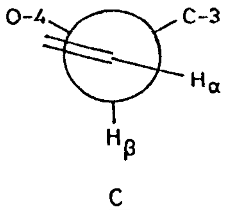
A prerequisite to understanding the stereochemical path of a reaction is to know the conformation of the starting material. The first conformational studies on the formyl group of aldehydosugars were undertaken by Horton[17] who noted the generally very small value of the $^3J_{\alpha,\beta}$ coupling constant and proposed for these compounds conformations of the **A** and/or **B** types where the carbonyl group almost eclipses a large substituent of the β-carbon atom.



A



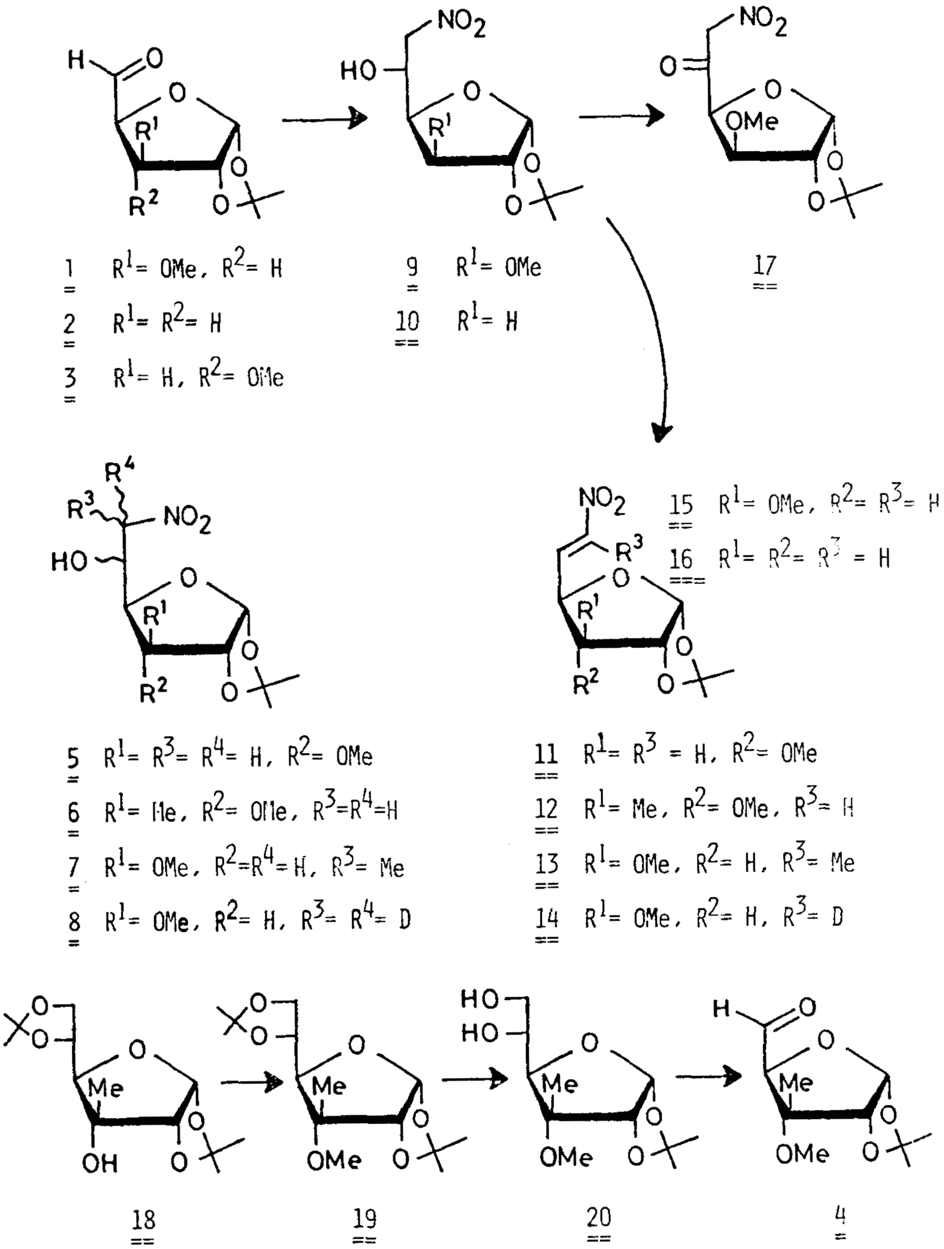
B



C

These early observations have been confirmed by the study of a large number of aldehydosugars (cf f. ex.[7,10]). In any case, conformers **A** and **B** are both in accordance with the observed coupling constant. These two conformers, degenerate regarding the

Scheme 1



1 R^1= OMe, R^2= H

2 R^1= R^2= H

3 R^1= H, R^2= OMe

9 R^1= OMe

10 R^1= H

17

15 R^1= OMe, R^2= R^3= H

16 R^1= R^2= R^3 = H

5 R^1= R^3= R^4= H, R^2= OMe

6 R^1= Me, R^2= OMe, R^3=R^4=H

7 R^1= OMe, R^2=R^4=H, R^3= Me

8 R^1= OMe, R^2= H, R^3= R^4= D

11 R^1= R^3 = H, R^2= OMe

12 R^1= Me, R^2= OMe, R^3= H

13 R^1= OMe, R^2= H, R^3= Me

14 R^1= OMe, R^2= H, R^3= D

18 19 20 4

$J_{\alpha,\beta}$ coupling constant, are stereochemically different as **A** presents the re face of its carbonyl to an outside attack, whereas **B** presents the si face. We have shown[18] that (E)-enoses bearing on their double bond a -M substituant adopt preferentially the conformation **C** very close to **A**. Given the similarities between such vinyl groups and a carbonyl, the same type of conformational equilibrium was a priori expected. That such was the case was established by NOE experiments (cf FIG. 1) in $CDCl_3$ and in CD_3OD solutions. So, when the reaction is stereospecific the exclusive product comes from an attack from the less sterically accessible face. Clearly, this rules out the simplistic hypothesis that the stereochemical issue of the reaction would only depend on which face of the double bond is facing outside in the most populated ground-state conformation. On the other hand, the different behaviour of **1** and **4** proves that the steric hindrance on the β face at C-3 is less important than the spatial distribution of the oxygen atoms. The simplest explanation would be that $O\text{-}C_4$ and, if present, an $O\text{-}C_3$ on the β face of the sugar promote an attack from inside the ring whereas, when present, an equatorial oxygen at C-3 allows a competitive pathway directing the nucleophile towards the si face of the carbonyl. The conjugate base of nitroethane gave **7** as a mixture of isomers.

The nitrosugars **5**, **6**, **8**, **9** and **10** were easily dehydrated via their O-acetates to the corresponding nitroenoses **11**, **12**, **14**, **15** and **16**. The classical work-up procedure[19] was improved by evaporating directly from the reaction mixture the excess of acetic anhydride and the acetic acid, which avoided the rehydration of the double bond which took place during the aqueous work-up of some of the compounds (e.g. **11**). Only the nitrosugars **7** resisted this procedure and we had to substitute their hydroxyl group with a chlorine atom[20] before the elimination step, carried out by chromatography on silica gel and leading to **13**. All the obtained enoses were of E configuration. This was proved by ^1H-NMR : a $^3J_{5,6}$ coupling constant larger than 13 Hz for **11**, **12**, **15** and **16**; a small (3.7 Hz) value of $^3J_{4,5}$ indicating a conformation

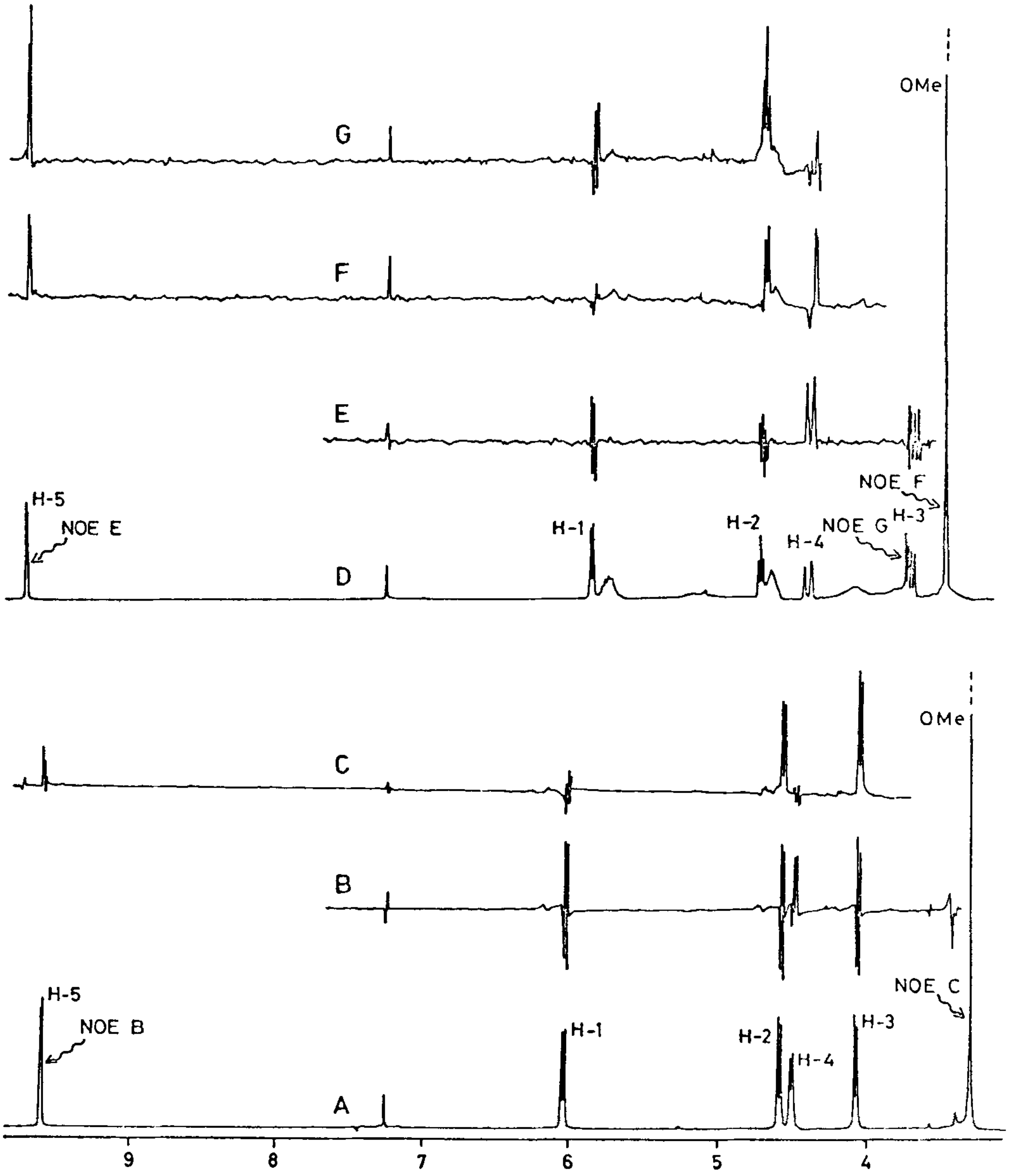


FIG. 1 : NOE experiments (200 MHz, $CDCl_3$) on aldehydosugars **1** (traces A-C) and **3** (traces D-G).

where the double bond eclipses C-4-O, exclusively compatible with a E configuration for **14**; NOE experiments showing mostly an enhancement of the signal of H-4 on irradiation of H_3C-7 for **13**. As shown in the Table 1, all nitroenoses bearing hydrogen atom on C-6 presented small value of $^3J_{4,5}$. This corresponds to the most stable eclipsed conformer[15] of E-enoses bearing an electron withdrawing group on their double bond.

In order to enlarge the synthetic possibilities of nitro sugars, we prepared compounds bearing another reactive functional group in the vicinity of the nitro group (Scheme 2). Amongst them, the keto derivative **17** was obtained in good yield by stochiometric ruthenium tetraoxide oxidation of **9**, the other classical oxidation procedures, Collins',[21] Moffatt's,[22] having failed. The methylene protons of **17** were exchanged in a few minutes in $D_2O/CHCl_3$.

Nitroenoses are useful starting materials for a number of polyfunctional compounds. Some reactions of the model compound **15** are described. For example, chain extension using the anion of 2-methyl-1,3-dithiane gave a mixture (2:3) of the two masked nitrouloses **21s** (slow-moving isomer on silica gel ether/hexane 2:1) and **21f** (fast-moving). Neither of these two compounds is in a pure conformational state around the C-4 - C-5 bond and **21f** adopts an unusual conformation. In these conditions, configurational assigments by NMR are very difficult even when using NOE and relaxation time experiments. Some data pertinent to this problem are collected in Table 2. Generally, when each of two vicinal carbon atoms bears one hydrogen atom and two large groups, an antiperiplanar conformation is expected. It is not the case here and, as has been shown in other occasions[23] in furanose chemistry, the orientation of C-3 substituents very often directs the C-4 - C-5 conformation. For the fast-moving isomer, one (**D**) of the two possible conformations is sterically forbidden whichever the configuration at C-5, whereas the second one is only sterically feasible if it is the small group which is placed on the sugar ring (**E**). As molecular models show that the

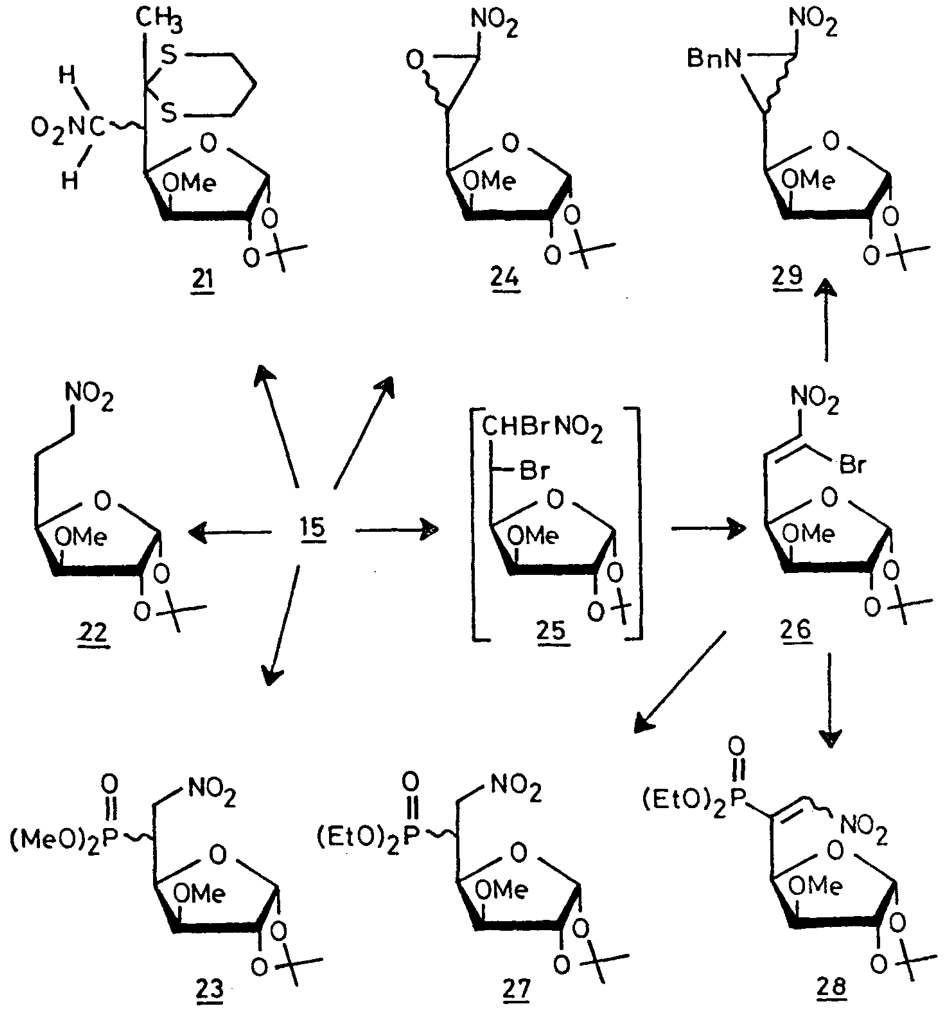
TABLE 1

^{1}H-NMR Data of some Nitro Sugars measured in CDCl$_3$ (Chemical Shifts in ppm from Me$_4$Si, coupling constants in Hz)

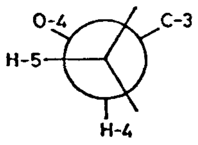
Compounds	Chemical Shifts						Coupling constants				
	H-1	H-2	H-3	H-4	H-5	H-6	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
11	5.77	4.66	3.34	4.60	7.30	7.20	3.7	4.0	4.0	3.1	13.5
12	5.84	4.58	-	4.74	7.12[a]	7.25[a]	3.5	-	-	2.8[a]	13.3[a]
13	5.97	4.66	3.80	4.84	7.15	-	3.7	0.0	3.3	7.3	-
15	5.96	4.63	3.87	4.90	7.33[a]	7.27[a]	3.7	0.0	3.3	3.2[a]	13.4[a]
16	5.91	4.81	2.40R 1.77S	4.91	7.30	7.27	3.5	0.0 4.1	4.7 10.7	1.7	13.2
17	6.05	4.60	4.10	4.75	-	5.56 5.44	3.3	0.0	3.5	-	-
26	6.00	4.64	4.00	4.93	7.71	-	3.7	0.0	3.3	7.0	-
(E)28	6.06	4.63	4.30	5.71	-	7.54	3.7	0.0	5.0	12.7	16.3[b]
(Z)28	5.91	4.67	?	5.50	-	7.43	4.0	0.0	?	?	34.0[b]

[a] measured in acetone-d6. [b] coupling phosphorus,H-6.

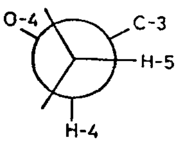
Scheme 2



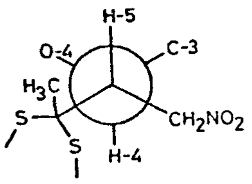
nitromethyl group is less sterically demanding than the dithiane ring, this speaks in favour of this fast-moving isomer having the L-*ido* configuration.



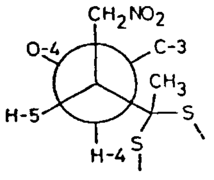
D



E



F



G

TABLE 2

Some ^{1}H-NMR data of **21s** and **21f**

Isomers	Protons	$^3J_{4,5}$	NOE	R_1° [a]	R_1 [b]	R_1/R_1° [c]
slow-	H-1		0	0.24 ± 0.01	0.31 ± 0.01	1.29
moving	H-2		0		0.59 ± 0.37	
21s	H-3		10%		0.63 ± 0.02	
	H-4	6	5%	0.50 ± 0.04	0.67 ± 0.04	1.34
	H-5		5%	0.75 ± 0.03	0.83 ± 0.05	1.1
fast-	H-1		8%	0.34 ± 0.01	0.42 ± 0,01	1.25
moving	H-2		5%		0.55 ± 0,01	
21f	H-3		0		0.63 ± 0.01	
	H-4	1	16%	0.54 ± 0.02	0.70 ± 0.03	1.30
	H-5		0	0.64 ± 0.02	0.89 ± 0.01	1.39
	H-6a		10%			

[a] Selective relaxation rate. [b] Non selective relaxation rate.
[c] These figures are all inferior to the theoretical value[24] of 1.5 as noted[25] in some other cases.

For the slow-moving isomer ($J_{4,5}$ = 6.0 Hz) some of the antiperiplanar conformer (**F**) should participate in the conformational equilibrium. This is only possible for the *D-gluco* isomer. It seems even strange that the favourable **F** conformation is not exclusive and it is difficult to propose another conformation of similar stability; **G** could be a candidate if the C-S bonds were not staggered with the vicinal substituents. The NOE and relaxation measurements could be in accordance with this proposition which cannot be considered as definitely establishing the configuration of **21f** and **21s**.

Sodium borohydride reduction of **15** gave **22** whereas nucleophilic attack of **15** by trimethylphosphite in the presence of LiI gave a low yield (22%) of 23 as a mixture of epimers. A very high yield (90%) of a unique trans isomer of 24 was obtained on treating 15 with alkaline hydrogen peroxide.

The third-generation synthetic intermediate 26 was prepared in a 90% yield by bromination - dehydrobromination of 15. Its Z configuration could be inferred from the chemical shift of H-C-5 (Table 1). On treatment with trialkyl phosphite it gave, depending on the reaction conditions, the product of an addition-elimination (28, aprotic medium) or of an addition (nucleophilic)-substitution (electrophilic) (27, protic medium). Both 27 and 28 were obtained as mixtures of isomers, the E ($J_{P,6}$ = 16.3 Hz) isomer of 28 predominating over the Z ($J_{P,6}$ = 34 Hz) (E/Z ratio = 4).

From the reaction of benzylamine with 26 we isolated an unique (trans) isomer, albeit in poor yield (28%), of 29.

EXPERIMENTAL

General Methods. see ref. 26.

1,2-O-Isopropylidene-3-C-methyl-3-O-methyl-α-D-ribo-pentodialdofuranose (4). 4 was prepared from 20 (1.42 g, 5.6 mmol) by oxidative cleavage with sodium metaperiodate . After distillation (105°, 10^{-1} mm Hg) 1.1 g (91%) of anhydrous 4 was obtained: Rf 0.45 (ether/hexane/MeOH 9:5:1); $/\alpha/_D^{25}$ + 51.6° (c 1.4, $CHCl_3$); UV (EtOH) : 212 (110); IR (film) : 3000, 2960 (CH), 1740 (C=O), 1390, 1380 (CMe_2), 1230, 1145; ^1H NMR (90 MHz, $CDCl_3$): 9.69 (d, 1, $J_{4,5}$ 1.0, H-5), 5.87 (d, 1, $J_{1,2}$ 3.3, H-1), 4.52 (d, 1, H-4), 4.36 (d, 1, H-2), 3.44 (s, 3, CH_3O), 1.60 (s, 3, CH_3-3), 1.30 and 1.24 (2s, 2x3, $C(CH_3)_2$); MS : 43 (100), 100 (78), 99 (68), 85 (61), 71 (51), 83 (47), 157 (44), 101 (32), 59 (27) ... 201 (7).

Anal. Calcd for $C_{10}H_{16}O_5$ (216.24) : C 55.55, H 7.46, Found : C 55.41, H 7.60.

General procedure for the preparation of nitroalcohols 5 to 7 and 9, 10 : To an ice cold solution of the corresponding aldehydosugar in MeOH (ca. 25 mL per g) was added nitromethane (or nitroethane,3 eq.) followed by sodium methoxide (2.9 eq.). After stirring for 2 h and 45 min, the medium was neutralized with Dowex 50 H$^+$, filtered and the solvent removed by distillation.

6-Deoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-*gluco* (and β-L-*ido*)-hexofuranoses (**5**). The above procedure applied to **3** gave **5** as a 1:1 mixture of D-*gluco* and L-*ido* isomers, in 87 % yield after treatment with active charcoal in ether: Rf 0.6 and 0.76 (ether/hexane/MeOH 18:5:2); mp 114°; UV (EtOH): 213 (2100); IR (KBr) : 3490 (OH), 3000, 2940 (CH), 1560 (NO_2), 1390 (CMe_2, NO_2), 1220, 1140; ^{1}H NMR (90 MHz): 5.8 (d + shoulder, 1, $J_{1,2}$ 3.7, H-1), 4.7 (t, 1, $J_{2,3}$ 3, H-2), 4.8-4.4 (m, 3, H-5, H-6), 3.95 (dd, 1, $J_{3,4}$ 9, H-3), 3.79 and 3.81 (2dd, 1, $J_{4,5}$ 3.9, H-4), 3.5 (*ca*. s, 3, OCH_3); 3.1 (broad s, OH), 1.55, 1.35 (2s, 2x3, $C(CH_3)_2$); MS : 248 (100), 172 (25), 152 (12), 87 (12), 85 (12), 249 (10), 43 (10), 127 (6), 59 (5).

Anal. Calcd for $C_{10}H_{17}NO_7$ (263.25) : C 45.63, H 6.51, N 5.32. Found : C 45.55, H 6.54, N 5.42.

6-Deoxy-1,2-O-isopropylidene-3-C-methyl-3-O-methyl-6-nitro-α-D-*allo*-(and β-L-*talo*)-hexofuranoses (**6**). The above procedure applied to **4** gave **6** as a 6:1 mixture of D-*allo* and L-*talo* isomers in 88 % yield : Rf 0.45 (ether/hexane/MeOH, 9:5:1); CD of the mixture θ_{271}, -3100°; UV (EtOH) : 233 (1800); IR (film): 3540 (OH), 3000, 2960 (CH), 1550 (NO_2), 1390, 1380 (CMe_2), 1230; ^{1}H NMR: 5.70 (d, 1, $J_{1,2}$ 3.7, H-1), 4.7-4.4 (m, 3, H-6, H-5), 4.33 (s, 1, H-2), 3.87 (d, 1, $J_{4,5}$ 8, H-4), 3.41 and 3.37 (2s, 2.6, 0.4, OCH_3), 3.0 (broad s, 1, OH), 1.58 (s, 3, CH_3-3), 1.36, 1.32 (2s, 2x3, $C(CH_3)_2$); MS : 100 (100), 262 (37), 101 (36), 43 (36), 85 (30), 117 (25), 59 (24), 45 (24), 187 (19), 161 (18).

Anal. Calcd for $C_{11}H_{19}NO_9$ (309.28) : C 47.65, H 6.91, N 5.05. Found : C 47.55, H 6.97, N 4.98.

6,7-Dideoxy-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-D (and L)-*glycero*- α-(and β-)D-*gluco* (and L-ido) heptofuranose (**7**).

The above procedure applied to **1**, using nitroethane, gave **7**, after 5 h of reaction and silica gel column chromatography in ether/hexane (2:1), in 49% yield as a mixture of isomers: mp 99.1-101° (ether/hexane); Rf 0.56 (ether/hexane, 2:1); UV (EtOH): 214 (2000); ^{1}H NMR (CDCl$_3$, 90 MHz) : 5.87 (d, 1, J$_{1,2}$ 3.7, H-1), 4.75 (m, 1, J$_{5,6}$ 2.3, J$_{4,5}$ 9.2, H-5), 4.65 (m, 1, H-6), 4.59 (d, 1, H-2), 4 (dd, 1, J$_{3,4}$ 3.2, H-4), 3.88 (d, 1, H-3), 3.45 (s, 3, OCH3), 2.8 (broad s, 1, OH), 1.6 (d, 3, J$_{6,7}$ 6.7, H-7), 1.48, 1.3 (2s, 2x3, C(CH$_3$)$_2$); MS : 83 (100), 85 (67), 262 (61), 173 (61), 87 (33), 43 (21), 59 (19), 91 (18), 57 (18).

Anal. Calcd for $C_{11}H_{19}NO_7$ (277.28) : C 47.65, H 6.91, N 5.05. Found : C 47.76, H 7.10, N 5.00.

6-Deoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-glucofuranose (**9**). **9** was prepared from **1** following the above procedure. After Al$_2$O$_3$ column chromatography in ether **9** (85 %) was obtained as a crystalline compound : mp 73.5-75.1° (lit.[8] syrup); Rf 0.44 (ether/hexane 3:1); /α /$^{22}_{D}$ -47.48° (c 1.2, CHCl$_3$) (lit.[8] -34.0°); CD θ$_{270}$ -8900°, θ$_{302}$ -11000°; UV (EtOH): 203 (4500); ^{1}H NMR (CD$_3$OD, 90 MHz) : 5.83 (d, 1, J$_{1,2}$ 3.7, H-1), 4.82 (m, J$_{4,5}$ 8, J$_{5,6b}$ = J$_{5,6b}$ 6, H-5), 4.66 (d, H-2), 4.64 (dd, J$_{6a,b}$ 8.4, Ha-6), 4.51 (dd, Hb-6), 4.04 (m, 1, J$_{3,4}$ 3.3 H-4), 3.82 (d, 1, H-3), 3.44 (s, 3, OCH$_3$), 1.44, 1.30 (2s, 2x3, C(CH$_3$)$_2$); IR (KBr) : 3480 (OH), 2970 (CH), 1590 (NO$_2$), 1390 (NO$_2$, CMe$_2$), 1293, 1273, 1220; MS: 248 (100), 173 (33), 85 (14), 87 (13), 152 (11), 43 (7), 59 (6), 103 (5).

Anal. Calcd for $C_{10}H_{17}NO_7$ (263.25) : C 45.63, H 6.51,N 5.32 Found : C 45.70, H 6.64, N 5.25.

3,6-Dideoxy-1,2-O-isopropylidene-6-nitro-α-D-ribo-hexofuranose (**10**). The above procedure applied to **2** gave 99% of **10** : mp 89.0-90.8°; Rf 0.54 (ether/hexane, 3:1); /α /$^{24}_{D}$ -12.42° (c 1.9, CHCl$_3$); CD θ$_{277}$ -2200°, θ$_{305}$ -1500°; UV (EtOH) : 214 (1800); IR (KBr) : 3470 (OH), 2990, 2950 (CH), 1560) (NO$_2$), 1388 (NO$_2$, CMe$_2$) 1225, 1065; ^{1}H NMR (90 MHz, CDCl$_3$) : 5.80 (d, 1, J$_{1,2}$ 3.6, H-1), 4.77 (t, 1, J$_{2,3s}$ 4.6, H-2), 4.6-4.35 (m, 3, H-5, H-6), 4.17

(ddd, 1, $J_{4,5}$ 5.3, $J_{4,3s}$ 10, $J_{4,3r}$ 4.5, H-4), 3.12 (broad s, 1, OH), (2.18 (dd, 1, $J_{3r,3s}$ 13.5, Hr-3), 1.85 (ddd, 1, Hs-3), 1.5, 1.33 (2s, 2x3, $C(CH_3)_2$); MS : 218 (100), 143 (40), 85 (13), 59 (12), 43 (12), 219 (10), 57 (4), 144 (3), 111 (3), 83 (3).

Anal. Calcd for $C_9H_{15}NO_6$ (233.22) : C 46.35, H 6.48, N 6.01. Found : C 46.35, H 6.52, N 6.09.

General procedure for the preparation of nitroenoses **11**, **12**, **15** and **16**. The corresponding nitroalcohol was dissolved at 0° in acetic anhydride (10 mL/g) and sodium acetate (2 g/g) was added. After about 2 days of stirring at room temp the solvent was evaporated, the residue suspended in ether,the mixture was filtered and the solvent evaporated to dryness to give the product.

(E)-5,6-Dideoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-ribo-hex-5-enofuranose (**11**). Dehydration of the nitroalcohol **5**, following the above general procedure gave 93% of the enose **11** after treatment with charcoal in ether : mp 84-89°; Rf 0.56 (ether/hexane, 3:1); $/\alpha/_D^{23}$ + 51.84° (c 1.6, $CHCl_3$); UV (EtOH) : 236 (6900); IR (KBr) : 3110 (unsatd CH), 3000 (CH), 1520 (NO_2), 1380 (CMe_2), 1355 (NO_2), 1215, 1150; ^{1} NMR (90 MHz, $CDCl_3$) : see Table 1 and 3.44 (s, 3, OCH_3), 1.5, 1.3 (2s, 2x3, $C(CH_3)_2$); MS : 85 (100), 230 (92), 115 (69), 129 (38), 59 (36), 58 (33), 43 (33), 86 (25), 112 (22), 61 (22).

Anal. Calcd for $C_{10}H_{15}NO_6$ (245.23) : C 48.98, H 6.17, N 5.71. Found : C 48.95, H 6.09, N 5.81.

(E)-5,6-Dideoxy-1,2-O-isopropylidene-3-C-methyl-3-O-methyl-6-nitro-α-D-ribo-hex-5-enofuranose (**12**). Dehydration of the nitroalcohol **6** following the above general procedure gave 83% of **12** : mp 115-116.2° (ether/hexane); Rf 0.63 (ether/hexane 5:1); $/\alpha/_D^{26}$ +55.0 (c 1.3, $CHCl_3$); UV (EtOH) : 233 (7200); IR : 3120 (unsatd CH), 3010, 3000 (CH), 1665 (C=C), 1530 (NO_2), 1390, 1385 (CMe_2); ^{1}H NMR (90 MHz, Acetone -d_6) : 7.25 (AB, $J_{5,6}$ 13.3, H-6), 7.15 (AB, $J_{4,5}$ 2.8, H-5); 5.84 (d, 1, $J_{1,2}$ 3.5, H-1), 4.75 (broad d, 1, H-4), 4.58 (d, 1, H-2), 3.40 (s, 3, OCH_3), 1,53, 1.36 (2s, 2x3, $C(CH_3)_2$), 1.16 (s, 3, CH_3-3); SM : 43 (100), 1129 (28), 100 (24), 99 (23), 59 (19), 157 (17), 83 (17), 68 (16), 75 (12), 244 (6).

Anal. Calcd for $C_{11}H_{17}NO_6$ (259.26), C 50.96, H 6.61, N 5.40. Found : C 50.98, H 6.59, N 5.35.

(E)-5,6,7-Trideoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-xylo-hept-5-enofuranose (**13**). A solution of the mixture of nitroalcohols **7** (2.3 g, 8.29 mmol), triphenylphosphite (4.35 g, 16.58 mmol) in 250 ml of CCl_4 was refluxed overnight under N_2. Filtration, evaporation of the solvent and silica gel column chromatography in ether/hexane 2:1, gave 87% of **13** (1.86 g, 7.17 mmol) : mp 78.9-80.6° (ether/hexane); Rf 0.6 (ether/hexane 2:1); /α /$^{23}_{D}$ -44.12° (c 1.3, $CHCl_3$); CD θ_{248} -4000°, θ_{295} + 4300°; UV (EtOH) : 244 (6700); IR (KBr) : 3120 (unsatd CH), 3000 (CH), 1525 (NO_2), 1390, 1380 (CMe_2), 1340 (NO_2), 1120; ^1H NMR (90 MHz, $CDCl_3$): see Table 1 and 3.40 (s, 3, OCH_3), 2.32 (d, 3, $J_{5,7}$ 1 Hz, H-7), 1,53, 1,36 (2s, 2x3, $C(CH_3)_2$); MS : 59 (100), 85 (94), 115 (54), 43 (51), 244 (49), 57 (49), 58 (47), 86 (46), 99 (33), 87 (24).

Anal. Calcd for $C_{11}H_{17}NO_6$ (259.26) : C 50.96, H 6.61, N 5.40. Found : C 51.09, H 6.47, N 5.45.

(E)-6-Deutero-5,6-dideoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-xylo-hex-5-enofuranose (**14**). To an ice cold solution of aldehyde **1** (2 g, 9.9 mmol), in 20 mL of ethyl acetate was added nitromethane-d_3 (2.4 mL, 4.47 mmol) and triethylamine (3.4 mL, 2.43 mmol). The medium was stirred 8 h at room temp and evaporated. The nitroalcohol **8** formed was not purified but directly dehydrated as above to produce 78% of **14** (1.9 g, 7.72). A 74% deuterium incorporation was obtained (NMR, MS).

(E)-5,6-Dideoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-xylo-hex-5-enofuranose (**15**). Dehydration of the nitroalcohol **9** following the above general procedure gave 58% of **25**, after silica gel column chromatography in ether/hexane 2:1 and recrystallization in ether/hexane : mp 55.3-56.1° (ether/hexane); Rf 0.4 (ether/hexane 3:1); / α /$_D^{25}$ -68.49° (c 1, $CHCl_3$); CD θ_{229} + 2800°, θ_{257} -3500°, θ_{305} +900°; UV (EtOH): 231 (8600); IR (KBr): 3098 (unsatd CH), 2990, 2940 (CH), 1649 (C=C), 1515 (NO_2), 1390, 1380 (CMe_2), 1350 (NO_2), 961 (HC=CH trans); ^{1}H NMR (90 MHz, acetone-d_6) : 7.33 (m, 1, $J_{5,6}$ 13.5, $J_{4,5}$ 3.2, H-5), 7.27 (m, 1, H-6), 5.92 (d, 1, $J_{1,2}$ 3.67, H-1), 4.98 (m, 1, $J_{3,4}$ 3.3, $J_{4,5}$ 3, H-4), 4.73 (d, 1, H-2), 3.97 (d, 1, H-3), 3.36 (s, 3, OCH_3), 1.42, 1.28 (2s, 2x3, $C(CH_3)_2$); MS : 230 (100), 85 (80), 117 (41), 59 (33), 129 (12), 112 (12), 231 (10), 198 (10), 118 (8), 122 (7).

Anal. Calcd for $C_{10}H_{15}NO_6$ (245.23) : C 48.98, H 6.17, N 5.71. Found : C 48.92, H 6.19, N 5.83.

(E) 3,5,6-Trideoxy-1,2-O-isopropylidene-6-nitro-α-D-erythro-hex-5-enofuranose (**16**). Dehydration of the nitroalcohol **10** following the above general procedure gave 83% of **16** : mp 95.1-96.7° (ether/hexane); Rf 0.74 (ether/hexane 2:1); / α /$_D^{22}$ -90.58° (c 0.9, $CHCl_3$); UV (EtOH): 236 (9000); IR (KBr) : 3140, 3060 (unsatd CH), 2998 (CH), 1675 (C=C), 1525 (NO_2), 1390, 1380 (CMe_2), 1370 (NO_2); ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1 and $J_{3r,3s}$ 13.5, 1.55, 1.38 (2s, 2x3, $C(CH_3)_2$); MS : 43 (100), 200 (44), 39 (36), 59 (28), 85 (15), 66 (9), 93 (7), 57 (7), 55 (6).

Anal. Calcd for $C_9H_{13}NO_5$ (215.21) : C 50.23, H 6.09, N 6.51. Found : C 50.19, H 6.03, N 6.51.

6-Dideoxy-1,2-O-isopropylidene-3-O-methyl-6-nitro-α-D-xylo-hex-1,4-furanos-5-ulose (**17**). To a methylene chloride solution of RuO_4, prepared according to ref. 27 from RuO_2 51% (5.6 g, 21.5 mmol), was added **9** (3.78 g, 14,37 mmol). After stirring one hour, excess RuO_4 was destroyed with isopropanol. Filtration, evaporation of the solvent, dissolution of the syrup in ether and filtration through a silica gel pad removed all the RuO_2. After evaporation 64% of **17** (2.41 g, 9.19 mmol) was obtained : mp 55.5-67.4°; Rf 0.6 (ether/hexane 3:1); / α /$_D^{24}$ -243,07° (c 0.75 $CHCl_3$); IR

(KBr) : 2980, 2940 (CH), 1745 (C=O), 1560 (NO_2), 1385 (CMe_2, NO_2), 1220, 1170; ^1H NMR (90 MHz, $CDCl_3$) : see Table 1 and $J_{6A,B}$ 15.3, 3.4 (s, 3, OCH_3), 1.5, 1.35 (2s, 2x3, $C(CH_3)_2$); MS : 173 (100), 87 (62), 85 (58), 59 (46), 115 (40), 130 (31), 57 (29), 246 (18), 101 (16), 149 (12).

Anal. Calcd for $C_{10}H_{15}NO_7$ (261.23) : C 45.98, H 5.79, N 5.36. Found : C 46.11, H 5.89, N 5.28.

1,2:5,6-Di-O-isopropylidene-3-C-methyl-3-O-methyl-α-D-allofuranose (**19**). To sodium hydride (60% dispersion in oil, 0.78 g, 22.1 mmol) washed with pet. ether was added dropwise, under N_2, a solution of the alcohol **18**[13] (4.91 g, 17.92 mmol) in dry DMF (50 mL). After 1 h of stirring, methyl iodide was added (2.22 mL). Excess hydride was destroyed by 2.5 h of contact with MeOH. Filtration on celite, extraction of the sugar with $CHCl_3$, evaporation and column chromatography gave 54% of pure **19** (2.79 g, 9.68 mmol); bp 75-80° (10^{-3} mm Hg); Rf 0.7 (ether/hexane 5:1); $/\alpha/_D^{25}$ +58,91° (c 1.4, $CHCl_3$); UV (EtOH) : 228 (137); IR (film) : 3000, 2960 (CH), 1380 (CMe_2), 1260, 1230, 1180, 1150; ^1H NMR ($CDCl_3$) : 5.62 (d, 1, $J_{1,2}$ 3.7, H-1), 4.24 (d, 1, H-2), 4.2-3.0 (m, 4, H-4, H-5, H-6), 3.37 (s, 3, OCH_3), 1.54, 1.38 and 1.30 (s, s, s, 3, 3, 6, 2 $C(CH_3)_2$), 1.18 (s, 3, CH_3-3); MS : 101 (100), 43 (87), 100 (85), 273 (51), 72 (38), 83 (33), 99 (31), 85 (30), 114 (23), 129 (18).

Anal. Calcd for $C_{14}H_{24}O_6$ (288.34) : C 58.32, H 8.39. Found : C 58.48, H 8.45.

1,2-O-Isopropylidene-3-C-methyl-3-O-methyl-α-D-allofuranose (**20**). A solution of **19** (2.33 g, 9.38 mmol) in methanol/water (22:58 mL) was brought to pH 2 with HCl N. After stirring 8 h at room temp, the medium was neutralized with a saturated solution of sodium bicarbonate, washed with hexane (2 x 70 mL) evaporated and the solid extracted with $CHCl_3$. Silica gel column chromatography in ether/hexane/MeOH (9:5:1) gave 72% of **20** (1.68 g, 6.77 mmol) as a solid : mp 99.1-100° (ether/hexane); Rf 0.28 (ether/hexane/MeOH

9:5:1); /α/$^{25}_{D}$ +85.25° (c 1.0 $CHCl_3$); UV (EtOH) : 229 (140), 259 (106); IR (KBr): 3480, 3390 (OH), 3000, 2940 (CH), 1398, 1380 (CMe_2), 1080; ^{1} NMR (90 MHz, $CDCl_3$): 5.70 (d, 1, $J_{1,2}$ 3.7, H-1), 4.31 (d, 1, H-2), 4.0-3.5 (m, 4, H-4, H-5, H-6), 3.43 (s, 3, OCH_3), 2.98 (d, 1, $J_{5,OH}$ 2.3, HO-5), 2.78 (t, 1, $J_{6,\ OH}$ 6, HO-6), 1.61, 1.37 (2s, 2x3, $C(CH_3)_2$), 1,31 (s, 3, CH_3-3); MS : 101 (100), 100 (86), 85 (24), 43 (20), 71 (17), 83 (14), 72 (10), 187 (9), 59 (9), 73 (8), 233 (4).

Anal. Calcd for $C_{11}H_{20}O_6$ (248.28) : C 53.22, H 8.12. Found : C 53.27, H 8.17.

Addition of 2-methyl-1,3-dithiane-2-yl carbanion onto **15**. To a solution of 2-methyl-1,3-dithiane (1.37 g, 13.4 mmol) in dry THF (100 mL), under N_2, metallated at -25° with butyllithium (14 mmol / 7 mL ether) in one hour a solution of **15** (3g, 12.2 mmol) in THF (50 mL) was added dropwise at -70°. The medium was stirred 2 h at -25°, hydrolysed with a saturated solution of NH_4Cl, decanted and extracted with ether (100 mL). Collecting, drying and evaporating the organic phases gave 3.65 g of a crude mixture of **21s** and **21f** in a ratio of 2:3 (low pressure liquid chromatography). They could be separated by silica gel column chromatography in ether/hexane (1:2).

5,6,7-Trideoxy-6-C-(1,3-dithian-2-yl)-1,2-O-isopropylidene-5-C-nitromethyl-3-O-methyl-α-D-gluco (or β-L-ido)-heptofuranose (**21s**) : Rf 0.64 (ether/hexane 2:1); /α/$^{26}_{D}$ -41.96° (c 1.5, $CHCl_3$); UV (EtOH) : 215 (3000), 243 (1200); IR (CCl_4) : 2950, 2940 (CH), 1555 (NO_2), 1387, 1377 (CMe_2), 1370 (NO_2), 1090; ^{1}H NMR (200 MHz, $CDCl_3$): 5.89 (d, 1, $J_{1,2}$ 4, H-1), 4.89 (dd, 1, $J_{5,5'a}$ 4.5, $J_{5'a,5'b}$ 15.5, H-5'a), 4,70 (dd, 1, $J_{5,5'b}$ 5, H-5'b), 4,70 (dd, 1, $J_{3,4}$ 3, $J_{4,5}$ 6, H-4), 4.60 (d, 1, H-2), 3.87 (ca. q, 1, H-5), 3.80 (d, 1, H-3), 3.30 (s, 3, OCH_3), 2.99 (m, 2, J_{gem} 15, $J_{eq,\ ax}$ 3.5, $J_{ax,\ ax}$ 10, $(SCH\text{-}\underline{H}_{ax})_2$), 2.78 (m, 2, $J_{eq,ax}$ 3, $J_{eq,eq}$ 6, $(SCH\text{-}\underline{H}_{eq})_2$), 2.03 (ttd, 1, J_{gem} 14.5, $SCH_2CH\text{-}\underline{H}_{eq}$), 1.90 (ttd, 1, $SCH_2CH\text{-}\underline{H}_{ax}$), 1.53 (s, 3, H-7), 1.30, 1.48 (2s, 2x3, $C(CH_3)_2$); MS: 133 (100), 379 (39), 106 (38), 134 (28), 87 (16), 59 (14), 205 (9), 363 (9), 206 (8), 92 (8).

Anal. Calcd for $C_{15}H_{25}NO_6S_2$ (379.50) : C 47.48, H 6.64, N 3.69, S 16.90. Found : C 47.77, H 6.36, N 3.48, S 16.90.

5,6,7-Trideoxy-6-C-(1,3-dithian-2-yl)-1,2-O-isopropylidene-5-C-nitromethyl-3-O-methyl-β-L-ido (or α-D-gluco)-heptofuranose (**21f**) : mp 166.1°; Rf 0.74 (ether/hexane 2:1); $/\alpha/_D^{25}$ -36.0° (c 1.1, $CHCl_3$); UV (EtOH) : 217 (2200), 245 (1100); IR (KBr): 3000, 2920 (CH), 1565 (NO_2), 1385, 1375 (CMe_2), 1090, 1015; ^1H NMR (200 MHz, $CDCl_3$) : 5.89 (d, 1, $J_{1,2}$ 4.0, H-1), 4.88 (m, $J_{5,5'a}$ 4.2, $J_{5'a,5'b}$ 16, Ha-5'), 4.88 (dd, $J_{3,4}$ 3.2, $J_{4,5}$ 1, H-4), 4.6 (m, $J_{5,5'b}$ 4, Hb-5'), 4.51 (d, 1, H-2), 3.67 (d, 1, H-3), 3.59 (m, 1, H-5), 3.29 (s, 3, OCH_3), 3.12, 2.95 (ddd, J_{gem} 16, $J_{ax, ax}$ 13, $J_{eq, ax}$ 3, SCH-H_{ax}), 2.65, 2.58 (td, 2x1, $J_{eq, eq}$ 6, $J_{eq, ax}$ 3.5, SCH-H_{eq}), 2.10 (m, 1, J_{gem} 14, SCH_2CH-H_{eq}), 1.83 (m, 1, SCH_2CH-H_{ax}), 1.35 (s, 3, H-7), 1.48, 1.30 (2s, 2x3, $C(CH_3)_2$); MS : 135 (100), 379 (79), 106 (45), 366) (28), 206 (21), 380 (14), 87 (13), 173 (13), 133 (10), 381 (10).

Anal. Calcd for $C_{15}H_{25}NO_6S_2$ (379.50) : C 47.48, H 6.64, N 3.69, S 16.90. Found : C 47.44, H 6.52, N 3.71, S 16.88 after correction for a 1.54% residue.

5,6-Dideoxy-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-α-D-xylo-hexofuranose (**22**). To a solution of **15** (1 g, 4.1 mmol) in EtOH (15 mL) was added $NaBH_4$ (0.23 g, 6.1 mmol). After 30 min under stirring the solvent was evaporated, the solid extracted with $CHCl_3$, washed with water, dried on Na_2SO_4 and evaporated to produce 66% of **24** (670 mg, 2.7 mmol) : bp 220° (0.3 mm Hg); Rf 0.66 (ether/hexane 3:1); $/\alpha/_D^{21}$ -44.62° (c 1.15, $CHCl_3$); UV (EtOH): 213 (2200); IR (film) : 3000, 2960 (CH), 1555 (NO_2), 1380 (CMe_2, NO_2), 1220, 1170, 1120; ^1H NMR (90 MHz; $CDCl_3$) : 5.85 (d, 1, $J_{1,2}$ 3.7, H-1), 4.55 (d, 1, H-2), 4.54 (t, 2, $J_{5,6}$ 7, H-6), 4.25 (dt, 1, $J_{3,4}$ 3.33, $J_{4,5}$ 6.7, H-4), 3.63 (d, 1, H-3), 3.41 (s, 3, OCH_3), 2.37 (q, 2, H-5), 1.47, 1.31 (2s, 2x3, $C(CH_3)_2$); MS: 43 (100), 59 (72), 85 (70), 58 (39), 84 (38), 40 (32), 57 (31), 232 (31), 86 (30), 55 (28).

Anal. Calcd for $C_{11}H_{17}NO_6$ (259.26) : C 48.58, H 6.93, N 5.66. Found : C 48.63, H 6.92, N 5.80.

5,6-Dideoxy-5-C-dimethoxyphosphoryl-1,2-O-isopropylidène-3-O-methyl-6-C-nitro-α-D-gluco(and β-L-ido)-hexofuranoses (23). Trimethylphosphite (20 mL) was added to 15 (1.18 g, 4.8 mmol) and lithium iodide (3.18 g, 23 mmol). After vigorous stirring of the reaction mixture for 20 min, 10 mL of 0.1 N H_2SO_4 were added. Extraction with $CHCl_3$ (3 x 50 mL), drying, evaporating, silica gel column chromatography in ether/hexane (5:1), and distillation gave 22% of 22 (370 mg, 1.04 mmol) as a mixture of isomers. The main isomer crystallized at - 20° : mp 72.5-75.2° (ether/hexane); bp 200° (10^{-5} mm Hg); Rf 0.76 (ether/MeOH 10:1); $/\alpha/_D^{26}$ -57.63° (c 0.68, $CHCl_3$); IR (film): 3000, 2960 (CH), 1560 (NO_2), 1460, 1380 (NO_2, CMe_2) 1260 (P=O), 1225; ^{1}H NMR (200 MHz, $CDCl_3$) : 5.87 (d, 1, $J_{1,2}$ 4, H-1), 4.8-4.7 (m, 2, H-6), 4.57 (m, $J_{4,P}$ 3, $J_{4,5}$ 7, $J_{4,3}$ 3, H-4), 4.54 (d, H-2), 3.75 (H-3), 3.80 (d, 6, $J_{H,P}$ 11, $P(OCH_3)_2$), 3.55 (m, 1, $J_{5,P}$ 23, $J_{5,6a}$ = $J_{5,6b}$ 7, H-5), 3.40 (s, 3, OCH_3), 1.5, 1.35 (2s, 2x3, $C(CH_3)_2$; MS : 85 (100), 340 (96), 308 (94), 337 (57), 109 (53), 270 (50), 59 (49), 166 (37), 100 (37), 84 (36).

Anal. Calcd for $C_{12}H_{22}NO_9P$ (355.28) : C 40.57, H 6.24, N 3.94, P 8.72. Found : C 40.69, H 6.44, N 3.79, P 8.73.

Trans 2-(1,2-O-isopropylidene-3-O-methyl-α-D-xylofuranos-4-yl)-3-nitrooxirane (24). A solution of 15 (300 mg, 1.2 mmol) and H_2O_2 (1.5 mL) in EtOH (25 mL) was brought to pH 8 with NaOH 1N. After stirring 90 min zinc dust was added and the solvent evaporated. The solid was dissolved in water (50 mL) and extracted with ether (2 x 200 mL). The organic phase was dried and evaporated to produce 90 % of 24 (310 mg, 1.18 mmol): mp 95.0-96.9° (ether/hexane); Rf 0.8 (ether/hexane); $/\alpha/_D^{21}$ -93.75° (c 1.3, $CHCl_3$); UV (EtOH): 219 (2600); IR (KBr) : 2990, 2940 (CH), 1565 (NO_2), 1380 (NO_2, CMe_2), 1220, 1160, 1070; ^{1}H NMR (200 MHz, $CDCl_3$): 5.95 (d, 1, $J_{1,2}$ 3.8, H-1), 5.50 (s broad, 1, H-6), 4.65

(d, 1, H-2), 4.25 (t, 1, $J_{3,4}$ 3.6, $J_{4,5}$ 4, H-4), 3.9 (d, 1, H-3), 3.75 (dd, 1, $J_{5,6}$ 1, H-5), 3.45 (s, 3, OCH_3), 1.5, 1.35 (2s, 2x3, $C(CH_3)_2$); MS : 43 (100), 246 (38), 85 (35), 59 (34), 87 (25), 71 (21), 58 (17), 57 (16), 109 (14), 115 (14).

Anal. Calcd for $C_{10}H_{15}NO_7$ (261.23) : C 45.98, H 5.79, N 5.36. Found : C 45.94, H 5.62, N 5.36.

(Z)-6-Bromo-5,6-dideoxy-1,2-O-isopropylidene-3-O-methyl-α-D-xylo-hex-5-enofuranose (**26**). To a solution of bromine (250 mg, 1.56 mmol) in CCl_4 (1.5 mL) was added a solution of **15** (310 mg, 1.28 mmol) in CCl_4 (5 mL). After stirring 90 min, a suspension of Ag_2CO_3 (2 g, 7.25 mmol) in acetonitrile (11 mL) was added. After stirring an extra 2 h, the solid was filtered off, the solution evaporated, the syrup residue dissolved in $CHCl_3$, washed with a saturated solution of $NaHCO_3$ and dried. Evaporation of the solvent brought **26** to crystallization in a 90% yield : mp 50.7-54° (hexane); Rf 0.7 (ether/hexane 2:1); / α /$^{25}_{D}$ -72.03° (c 1.4, $CHCl_3$); UV (EtOH) 265 (350); ^1H NMR (90 MHz, $CDCl_3$) : see Table 1 and 3.4 (s, 3, OCH_3), 1.54, 1.35 (2s, 2x3, $C(CH_3)_2$); ^{13}C NMR : 132.32 (C-5), 130.36 (C-6), 112.26 ($\underline{C}Me_2$), 105.36 (C-1), 85.22 (C-2), 81.75 (C-3), 79.23 (C-4), 58.23 (OCH_3), 26.92, 26.24 ($C\underline{Me}_2$); MS : 85 (100), 59 (69), 115 (62), 43 (59), 310 (52), 308 (50), 58 (44), 86 (29), 202, 98 (21).

Anal. Calcd for $C_{10}H_{14}BrNO_6$ (324.14) : C 37.06, H 4.35, Br 24.65, N 4.32. Found : C 37.35, H 4.25, Br 24.90, N 4.34.

5,6-Dideoxy-5-C-diethoxyphosphoryl-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-α-D-gluco-and β-L-ido-hexofuranoses (**27**). To a solution of **26** (570 mg, 1.75 mmol) in EtOH (25 mL) cooled to -65° was added, under N_2, triethylphosphite (906 mg, 5.45 mmol) in EtOH (5 mL). The medium was stirred 5 h at that temp and then 2 h at room temp. Evaporation and silica gel column chromatography in ether/hexane/MeOH (18:5:2) gave 59% of **27** (380 mg, 1.03 mmol) as a 1 to 3 mixture of isomers: Rf 0.55 (ether/hexane/MeOH 18:5:2); UV (EtOH): 210 (1450); IR (film) : 3000, 2950 (CH), 1560 (NO_2), 1390, 1380 (CMe$_2$, NO$_2$), 1260 (P=O), 1220; ^{1}H NMR (200 MHz, CDCl$_3$, main isomer) : 5.87 (d, 1, $J_{1,2}$ 4, H-1), 4.8-4.7 (m, 2, H-6), 4.57 (m, $J_{4,P}$ 8, $J_{3,4}$ 3, $J_{4,5}$ 6, H-4), 4.56 (H-2), 4.16 (quint, 4, $J_{H,H}$ = $J_{H,P}$ 7.5, P(OCH$_2$-)$_2$), 3.38 (d, 1, H-3), 3.6 (dq, 1,$J_{5,P}$ 23, H-5), 3.37 (s, 3, OMe), 1.5, 1.34 (2s, CMe$_2$), 1.34 (t, P(OCH$_2$C$\underline{H}_3$)$_2$); MS: 240 (100), 193 (58), 206 (28), 247 (18), 165 (18), 85 (18), 109 (16), 336 (14), 260 (14), 137 (14), 368 (9).

Anal. Calcd for $C_{14}H_{26}NO_9P$ (383.34) : C 43.87, H 6.84, N 3.65, P 8.08. Found: C 43.99, H 7.02, N 3.53, P 8.24.

(*E* and *Z*)-*5,6-Dideoxy-5-C-(diethylphosphoryl)-3-O-methyl-6-C-nitro*-α-D-xylo-*hex-5-enofuranose* (**28**). To an ice cold solution of **26** (740 mg, 2.28 mmol) in dry toluene (10 mL) was added, under an inert atmosphere, a solution of triethylphosphite (1.19 mL) in toluene (2 mL). After stirring 90 min, the solvent was removed. Thick layer chromatography in ether/hexane/MeOH (9:5:1) gave 30% of **28** (260 mg, 0.62 mmol) as a 4:1 mixture of *E* : *Z* isomers : Rf 0.4 (ether/hexane/MeOH 9:5:1); UV (EtOH) : 232 (3900); /α/$^{21}_{D}$ - 75.21° (c 0.7, CHCl$_3$) (indicative value); IR (film) : 3000, 2950 (CH), 1550, 1540 (NO$_2$), 1380 (CMe$_2$, NO$_2$), 1260 (P=O), 1170; ^{1}H NMR (90 MHz, CDCl$_3$) : (*E*)-**28** see Table 1 and 4.2 (q, $J_{4,H}$ = $J_{H,P}$ 7.3, P(OCH$_2$-)$_2$), 3.3 (s, 3, OCH$_3$), 1.5-1.3 (m, 12, C(CH$_3$)$_2$, (C$\underline{H}_3$CH$_2$O)$_2$P); ^{13}C NMR : (*E*)-**28** 144.62 (d, $J_{C,P}$ 15.82, C-6), 138.20 (d, $J_{C,P}$ 169.54, C-5), 112.65 ($\underline{C}$Me$_2$), 105.86 (C-1), 85.97, 82.47 (C-2, C-3), 79.72 (C-4), 63.75-63.18 (P(O$\underline{C}$H$_2$CH$_3$), 58.46 (OCH$_3$), 27.38, 26.68 (C(C$\underline{H}_3$)$_2$), 16.32, 16.25 (P(OCH$_2$C$\underline{H}_3$)$_2$); MS : 85 (100), 43 (56), 59 (31), 115 (29), 238 (22), 55 (20), 51 (19), 58 (14), 366 (1), 381 (0.1).

Anal. Calcd for $C_{14}H_{24}NO_9P$ (381.32) : C 44.10, H 6.34, N 3.67, P 8.12. Found : C 44.27, H 6.27, N 3.61, P 8.05.

(*Trans-1-Benzyl-2-(O-isopropylidene-1,2-O-methyl-3*-α-D-*xylofuranos-4-yl)-3-nitroaziridine* (**29**). To a solution of **26** (640 mg, 1.97 mmol) in acetonitrile (6 mL) was added, at 4° a solution of benzylamine (422 mg, 3.95 mmol) in CH$_3$CN (4 mL). After 12 h of stirring, the same quantity of reagent was added. Stirring at 4° was continued for 7 days. Evaporation of the solvent and thick layer chromatography in ether/hexane (3:1) gave 28% of **29** (190 mg, 0.54 mmol): Rf 0.72 (ether/hexane 3:1); $/ \alpha /^{22}_{D}$ -35.16 (c 1.02, $CHCl_3$); UV (EtOH) : 210 (5600); IR (film): 2995, 2950 (CH), 1555 (NO_2), 1375 (NO_2, CMe_2), 1220, 1165, 1125; ^1H NMR (90 MHz, $CDCl_3$): 7.31 (broad s, 5, Ph), 5.93 (d, 1, $J_{1,2}$ 3.5, H-1), 4.71 (d, 1, $J_{5,6}$ 1.3, H-6), 4.6 (d, 1, H-2), 4.29 (dd, 1, $J_{3,4}$ 3.3, $J_{4,5}$ 6.7, H-4), 4.25, 3.95 (AB, 2, $J_{A,B}$ 14, $PhC\underline{H}_2$), 3.81 (d, 1, H-3), 3.27 (dd, 1, H-5), 1.48, 1.32 (2s, 2x3, $C(CH_3)_2$); MS : 91 (100), 304 (11), 92 (9), 115 (9), 85 (9), 43 (7), 162 (6), 246 (6), 143 (5), 87 (5).

Anal. Calcd for $C_{17}H_{22}N_2O_6$ (350.37) : C 58.28, H 6.33, N 8.00. Found: C 58.38, H 6.54, N 8.04.

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