Preparation of Methyl 2,3-Anhydro- and 2,3-*O*-Sulfinylfuranosides from Unprotected Furanosides Using the Mitsunobu Reaction

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Abstract: A new two step procedure for the synthesis of methyl 2,3-anhydro-α-D-lyxofuranoside and methyl 2,3-anhydro-β-D-ribofuranoside from D-xylose involving the intramolecular Mitsunobu reaction is presented. Likewise, methyl 2,3-anhydro-α-L-lyxofuranoside is obtained from L-arabinose. Cyclic sulfites with D-*ribo* configuration, synthetic equivalents of the corresponding anhydrosugars, are prepared in three steps from D-ribose.

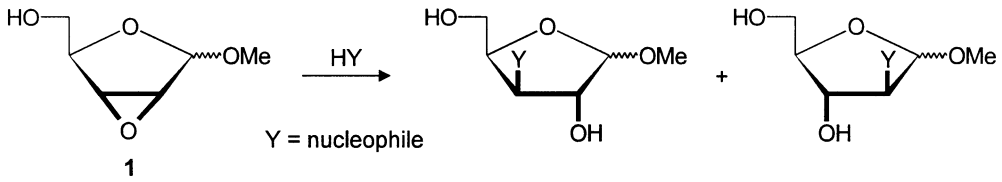
Key words: carbohydrates, epoxides, Mitsunobu reaction, sulfites, X-ray structure analysis

Strained carbohydrates, like 2,3- and 3,5-anhydrofuranosides, are important compounds since the oxirane- or oxetane substructure can be cleaved easily by various nucleophiles to yield pentofuranosides, exhibiting a configuration which depends on the anhydrosugar that was used as starting material[1] (cf. e. g., Scheme 1). The same is true for the corresponding cyclic sulfites or sulfates, which, due to their good leaving groups, also readily react with nucleophiles.[2] The regioselectivity of the nucleophilic attack depends on the kind of anomer, the nature of the nucleophile and of the reaction conditions.

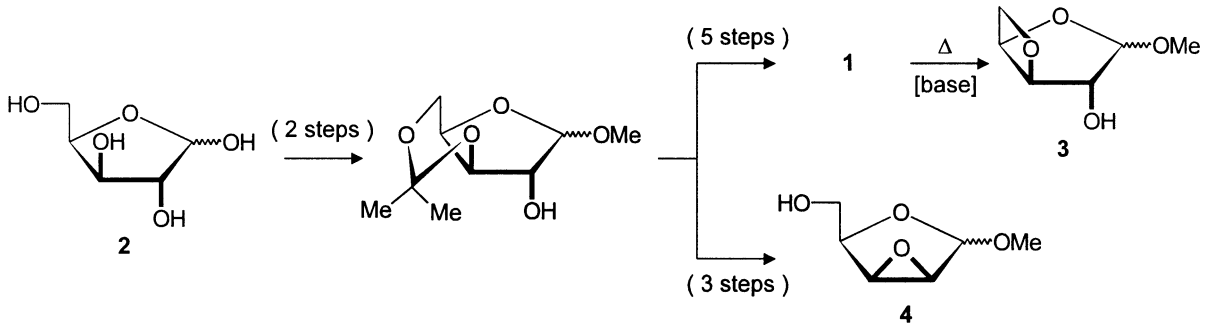
Several steps are however necessary to prepare these anhydrofuranosides. The synthesis of methyl 2,3-anhydro-D-lyxofuranoside (**4**)[3] and methyl 2,3-anhydro-D-ribofuranoside (**1**)[1] from D-xylose (**2**) requires five or seven steps, respectively. 3,5-Anhydro-D-xylofuranoside (**3**)[4] is prepared from **1** in an eighth step (Scheme 2).

Although the yields of the individual steps are generally high, a more facile synthesis is desirable. Since it has been shown that 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose **6** can be prepared from **2** via 1,2-*O*-isopropylidene-α-D-xylofuranose (**5**) by use of the Mitsunobu reaction[5] (Scheme 3), we have now investigated an analogous sequence using unprotected methyl pentofuranosides and designed alternatives to the multistep procedures for the preparation of 2,3-anhydro-pentofuranosides.

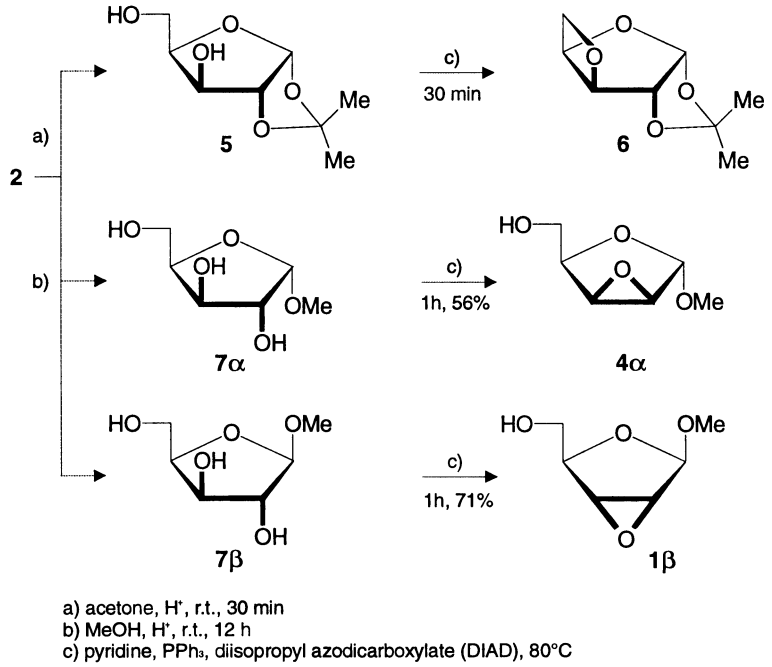
Methyl pentofuranosides were prepared according to the procedure described by Anker et al. for xylose[3] to give anomeric mixtures in good yields. The anomers could be separated by column chromatography. Only D-lyxose gave low yields because the formation of pyranosides was favoured.



Scheme 1



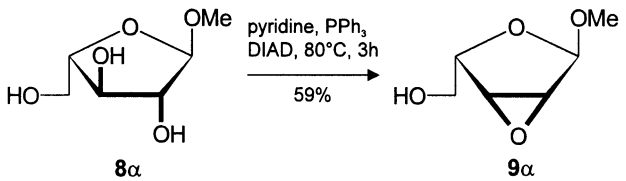
Scheme 2



Scheme 3

When the Mitsunobu reaction was performed using the methyl D-xylofuranosides **7** as starting compounds, the expected oxetanes **3** were not obtained. Instead, the oxiranes **1**β and **4**α were formed. Surprisingly, not even traces of the corresponding anomers **1**α or **4**β could be detected, indicating that **7**α exclusively leads to the *lyxo*-configurated product **4**α, whereas the corresponding β-anomer **7**β exclusively leads to the *ribo*-configurated product **1**β (Scheme 3). If the anomeric mixture of methyl D-xylofuranosides **7** is used as starting material the same product mixture, **1**β plus **4**α, is formed according to the NMR spectrum. The separation of the two products is, however, difficult and separation of the anomers **7**α and **7**β before performing the Mitsunobu reaction is favourable.

Under the same conditions, methyl α-L-arabinofuranoside (**8**α) yielded methyl 2,3-anhydro-α-L-lyxofuranoside (**9**α), the enantiomer of **4**α (Scheme 4), whereas **8**β did not react at all and was recovered nearly quantitatively. The methyl ribofuranosides (**10**) led to complex product mixtures under the Mitsunobu conditions.



Scheme 4

The synthesized anhydrosugars are identical with those prepared in the conventional way.[1,3] Since it was possible to crystallize **4**α and its α-L-enantiomer **9**α, we could perform an X-ray diffraction study of both enantiomers that confirmed our results (Figure 1).

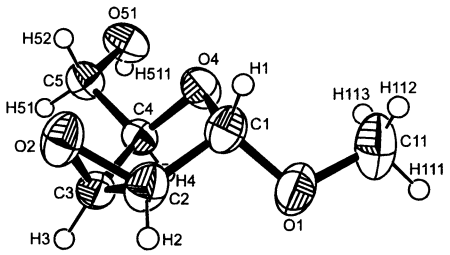


Figure 1 ORTEP view of the X-ray diffraction structure of **4**α with atom numbering. Thermal ellipsoids are drawn at the 50% probability level.

In a more complicated way but also using the Mitsunobu reaction Martin et al.,[6] synthesized methyl 2,3-anhydro-α-D-lyxofuranoside (**4**α) from methyl α-D-arabinofuranoside. They proposed a 1,3,2-dioxa-λ^5-phosphorinane as intermediate (Figure 2). An analogous intermediate could explain the formation of **1**β starting from **7**β. Of course these intermediates are reasonable but the inability of **8**β to react cannot be explained. Furthermore the formation of **4**α from **7**α can hardly be explained because the corresponding 1,3,2-dioxa-λ^5-phosphepane intermediate seems to be unlikely in our opinion. Obviously the detailed mechanism of the intramolecular Mitsunobu reaction is not fully understood.

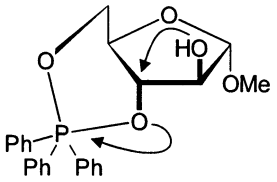


Figure 2 A proposed 1,3,2-dioxa-λ^5-phosphorinane intermediate [**6**].

As mentioned earlier, cyclic sulfites are useful synthetic equivalents of anhydrosugars.[2] These compounds can easily be obtained from ribofuranoside derivatives if their primary hydroxy groups are protected.[7] Since we were interested in the synthesis of thioanhydrosugars, which can be prepared by cleavage of thioacetates and subsequent intramolecular nucleophilic attack on a leaving group,[8] we used the thio Mitsunobu reaction to introduce an acetylthio group at the 5-position of **10**β. This reaction was highly chemoselective. No reaction at the secondary hydroxy groups was observed. The reaction of **11**β with thionyl chloride led to a diastereomeric mixture of two sulfites **12**β, which could not be separated chromatographically. However the minor *exo*-diastereomer (*exo*-**12**β) crystallized from methanol (Scheme 5). The structure of this isomer was confirmed by an X-ray diffraction study (Figure 3).

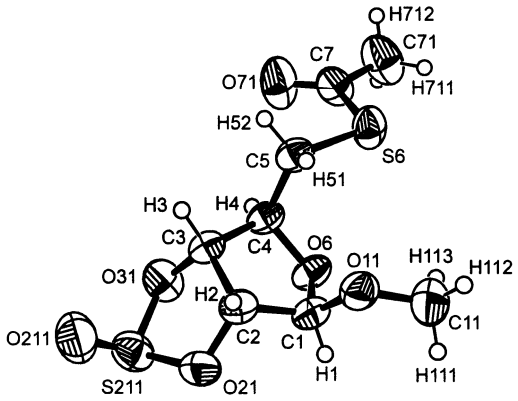


Figure 3 ORTEP view of the X-ray diffraction structure of *exo*-**12**β with atom numbering. Thermal ellipsoids are drawn at the 50% probability level.

Mps were determined by the use of an Electrothermal apparatus (values are corrected). IR spectra were measured with an ATI Mattson Genesis spectrometer. NMR spectra were recorded with a Bruker AMX 400 spectrometer. Chemical shifts (ppm) are related to TMS (^{1}H and ^{13}C). Standard correlation techniques (H,H-COSY, HMQC, HMBC, DEPT) were used for assignments. Mass spectra were measured on Varian CH 7 (EI, 70 eV) and VG Analytical 70−250 S (HRMS) apparatus. Optical rotations were measured on a Perkin−Elmer Polarimeter 341. TLC was carried out on E. Merck PF_{254} foils (detection: UV light, EtOH-H_2SO_4 spray / 200 °C), and column chromatography on E. Merck Kieselgel 60 (70−230 mesh). Solvents were purified and dried according to standard laboratory procedures.[9]

X-ray Structure Analysis

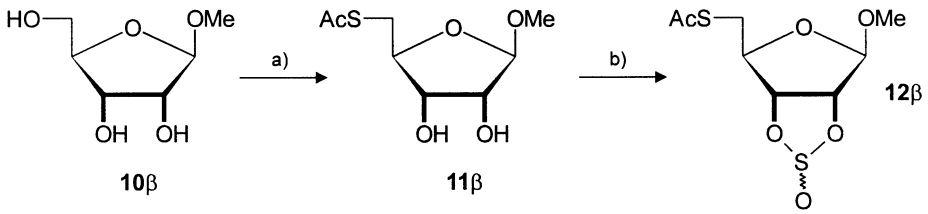
The crystal data and a summary of experimental details for **4**α, **9**α and *exo*-**12**β are given in Table 1. In all cases data collection was performed on a KappaCCD Nonius diffractometer, with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) in the rotation Φ scan mode at a temperature of 293(2) K. Cell parameters were determined by least-squares refinement of the angular settings of 1344 reflections with Θ = 1.00°−27.48° (**4**α), 267 reflections with Θ = 1.00°−27.48° (**9**α) and of 646 reflections with Θ = 11°−25° (*exo*-**12**β). The structures were solved by direct methods using the SIR-97[10] program, and refined by full-matrix-block least-squares on F^2 using all data and the SHELXL-97[11] program. Hydrogen positions were obtained by difference Fourier synthesis and / or geometrical methods. Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Tel.+441223336408, Fax +441223336033, E-mail: deposit@ccdc.cam.ac.uk under the deposition numbers CCDC-142691 (**4**α), 142692 (**9**α) and 142690 (*exo*-**12**β).

Methyl Aldopentofuranosides; General Procedure

The aldopentose (5.00 g, 33.3 mmol) was added to a methanolic HCl solution prepared from acetyl chloride (1 mL, 14.0 mmol) and MeOH (100 mL). When all the starting material was consumed (TLC detection), Ag_2CO_3 (3.0 g, 10.9 mmol) was added and the reaction mixture was stirred over night. After filtration through Celite, the solvent was evaporated and the resulting residue was purified by column chromatography (silica gel, EtOAc/EtOH, 3:1) in order to separate the anomers.

Mitsunobu Reaction of Methyl Aldopentofuranosides

Diisopropyl azodicarboxylate (1.2 mL, 5.97 mmol) was added to a solution of triphenylphosphine (1.58 g, 6.03 mmol) in dry pyridine (17 mL). After 10 min., a solution of methyl aldopentofuranoside (0.50 g, 2.32 mmol) in pyridine (3 mL) was added. Then the reaction mixture was stirred at 80 °C until the starting material was consumed (TLC monitoring, 1 h for **7**α/**7**β and 3 h for **8**α). After vacuum evaporation of the solvent, the residue was filtered through



a) THF, AcSH, PPh_3, DIAD, 0°C, 12 h, 71%
b) THF, NEt_3, $SOCl_2$, -20°C, 3 h, 87%

Scheme 5

Table 1 Crystal Data and Structure Refinement for **4**α, **9**α and *exo*-**12**β

	4α	**9**α	*exo*-**12**β
Molecular formular	$C_6H_{10}O_4$	$C_6H_{10}O_4$	$C_8H_{12}O_6S_2$
Molecular weight (g Mol^{-1})	146.14	146.14	268.30
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
Unit cell dimensions	a = 8.908(1) Å b = 4.444(1) Å c = 9.138(1) Å α = γ = 90° β = 100.81(1)°	a = 8.905(1) Å b = 4.444(1) Å c = 9.139(1) Å α = γ = 90° β = 100.80(1)°	a = 11.308(1) Å b = 4.588(1) Å c = 12.433(1) Å α = γ = 90° β = 112.84(1)°
Volume (Å³)	355.33(1)	355.26(1)	594.46(15)
Z (molecules per cell)	2	2	2
Crystal size (mm^3)	0.47 × 0.21 × 0.11	0.38 × 0.25 × 0.22	0.35 × 0.28 × 0.22
θ Range for data collection (°)	2.27–27.29	2.27–27.57	1.78–25.00
Index ranges	$0 \le h \le 11$; $-5 \le k \le 5$; $-11 \le l \le 11$	$0 \le h \le 11$; $-5 \le k \le 5$; $-11 \le l \le 11$	$-13 \le h \le 13$; $-5 \le k \le 5$; $-14 \le l \le 14$
Reflections collected	7030	16507	3275
Independent reflections	1595	1591	2090
Reflections with $I \ge 2\sigma(I)$	1456	1438	2017
Refinement method	full-matrix-block least-squares on F^2	full-matrix-block least-squares on F^2	full-matrix-block least-squares on F^2
Function minimized	$\Sigma w(F_o^2-F_c^2)^2$, $w = 1/[\sigma^2(F_o^2)+(0.0776P)^2+0.0194P]$, where $P = (F_o^2+2F_c^2)/3$	$\Sigma w(F_o^2-F_c^2)^2$, $w = 1/[\sigma^2(F_o^2)+(0.1032P)^2+0.0344P]$, where $P = (F_o^2+2F_c^2)/3$	$\Sigma w(F_o^2-F_c^2)^2$, $w = 1/[\sigma^2(F_o^2)+(0.0816P)^2+0.1233P]$, where $P = (F_o^2+2F_c^2)/3$
H-atom refinement	geom and difmap	geom and difmap	geom
Final R indices [$I \ge 2\sigma(I)$]	R_1 = 0.0341, wR_2 = 0.1028	R_1 = 0.0442, wR_2 = 0.1235	R_1 = 0.0381, wR_2 = 0.0980

silica gel (EtOAc) and then purified by column chromatography (silica gel, EtOAc). Compound **7**α yielded **4**α (0.19 g, 1.30 mmol, 56%) as colourless needles; mp: 83 °C (lit.[1] mp: 78–80 °C); $[\alpha]_D^{20}$ 84.9° (c 1.0, $CHCl_3$) [lit.[1] $[\alpha]_D^{20}$ 65.7 (c 0.42, H_2O)]; R_f 0.58 (EtOAc). Compound **7**β yielded **1**β (0.24 g, 1.64 mmol, 71%) as a colourless syrup; bp: 72 °C (0.05 mm) [lit.[12] bp: 48 °C (0.005 mm)]; $[\alpha]_D^{20}$ −122.7° (c 1.0, $CHCl_3$) [lit.[12] $[\alpha]_D^{28}$ −109° (c 1.98, H_2O)];R_f 0.59 (EtOAc). Compound **8**α yielded **9**α (0.20 g, 1.37 mmol, 59%) as colourless needles; mp: 82 °C; $[\alpha]_D^{20}$ −83.9° (c 1.0, $CHCl_3$); R_f 0.57 (EtOAc). Compound **9**β did not react even after prolonged stirring under reflux. Compounds **10**α and **10**β yielded complex mixtures. The spectroscopical data of **4**α and **1**β were in accordance with those reported in the literature.[1,3,12]

Methyl 5-*S*-Acetyl-5-thio-β-D-ribofuranoside (11β)

A cooled (0 °C) solution of methyl β-D-ribofuranoside (7.75 g, 47.2 mmol) and freshly distilled thioacetic acid (4.3 mL, 60.4 mmol) in THF (290 mL) was added to a cooled (0 °C) mixture of triphenylphosphine (14.79 g, 56.4 mmol) and diisopropyl azodicarboxylate (10.8 mL, 55.5 mmol) in THF (190 mL). The reaction mixture was allowed to warm to r.t. and stirred over night. After evaporation of the solvent, the residue was suspended in H_2O (100 mL) and filtered. The filtrate was washed with light petroleum:Et_2O (1:1) (5 × 50 mL each), then saturated with NaCl and extracted with $CHCl_3$ (5 × 100 mL). After drying ($MgSO_4$), filtration, and evaporation, the residue was purified by column chromatography (silica gel, EtOAc, R_f 0.65) to yield **11**β (7.47 g, 33.6 mmol, 71%) as a pale yellow syrup.

IR (film): ν = 3407 (O-H), 2931, 2834 (C-H), 1692 (C=O), 1196, 1128, 1103, 1029 (C-O) cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ = 2.40 (s, 3H, SAc), 3.13 (dd, 1H, H-5), 3.30 (dd, 1H, H-5'), 3.36 (s, 3H, OMe), 4.04 (d, 1H, H-2), 4.05–4.15 (m, 2H, H-3, H-4), 4.73 (HDO), 4.85 (s, 1H, H-1). $J_{1,2}$ = 0, $J_{2,3}$ = 4.2, $J_{4,5}$ = 6.3, $J_{4,5'}$ = 4.4, $J_{5,5'}$ = 14.3 Hz.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.36 (SAc), 32.40 (C-5), 55.54 (OMe), 73.69 (C-3), 74.78 (C-2), 81.07 (C-4), 108.32 (C-1), 200.62 (C=O).

Table 2 Yields and R_f Values of Methyl Aldopentofuranosides

	α-anomer		β-anomer	
	Yield (%)	R_f	Yield (%)	R_f
D-xylose	45.6	0.53	54.3	0.58
D-ribose	20.0	0.47	70.9	0.63
L-arabinose	21.8	0.56	62.6	0.43
D-lyxose	3.2	0.59	0	–

Methyl 5-*S*-Acetyl-2,3-*O*-sulfinyl-5-thio-β-D-ribofuranoside (12β)

Et_3N (10.2 mL, 73.6 mmol) and a solution of thionyl chloride (2.7 mL, 37.2 mmol) in THF (7 mL) were added to a solution of methyl 5-*S*-acetyl-5-thio-β-D-ribofuranoside (4.02 g, 18.1 mmol) in THF (70 mL) at −20 °C. After 3 h, the reaction mixture was diluted with EtOAc (100 mL) and washed several times with brine (70 mL each). After drying ($MgSO_4$), filtration, and evaporation of the solvent, the residue was purified by column chromatography (470 g silica gel, Et_2O) yielding a diastereomeric mixture of the products (4.22 g, 87%, R_f 0.92) as a yellow solid. According to the ^{1}H NMR spectrum, the ratio of the two diastereomers was 125:100 in favour of *endo*-**12**β. The minor isomer *exo*-**12**β crystallized from MeOH as colourless needles (mp: 113 °C). Its structure was verified by an X-ray diffraction study.

Table 3 ^{1}H NMR Data [400 MHz, D_2O, δ (ppm), *J* (Hz)] of Methyl Aldopentofuranosides

Furanoside	Nr.	1-H	2-H	3-H	4-H	5-H	5'-H	OMe	HDO	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
α-D-xylo	**7**α	4.78	3.92	4.07	4.03	3.48	3.55	3.23	4.58	4.5	5.7	0	6.0	3.8	12.2
β-D-xylo	**7**β	4.80	4.02	4.13	4.26	3.64	3.75	3.30	4.69	0	1.7	5.1	7.7	4.4	11.9
α-D-ribo	**10**α	5.18	4.30	3.92	4.29	3.85	3.93	3.62	4.94	4.4	6.3	3.4	4.6	3.4	12.3
β-D-ribo	**10**β	5.07	4.20	4.33	4.18	3.78	3.97	3.57	4.92	0.9	4.8	6.9	6.5	3.4	12.3
α-L-arabino	**8**α	4.83	3.96	3.85	3.94	3.60	3.72	3.32	4.65	1.5	3.4	5.9	5.8	3.4	12.3
β-L-arabino	**8**β	4.85	4.10	3.96	3.84	3.58	3.72	3.38	4.71	4.6	7.9	7.0	7.0	3.5	12.2
α-D-lyxo		4.83	3.99	4.21	4.13	3.62	3.70	3.32	4.66	3.7	4.8	ca. 4.3	6.8	4.3	11.9

Table 4 ^{13}C NMR Data [101 MHz, D_2O, δ (ppm)] of Methyl Aldopentofuranosides

Furanoside	Nr.	1-C	2-C	3-C	4-C	5-C	OMe
α-D-xylo	**7**α	102.38	77.05	75.29	78.61	60.83	55.95
β-D-xylo	**7**β	108.98	80.22	75.29	82.91	61.43	55.54
α-D-ribo	**10**α	105.25	73.18	71.77	86.58	63.61	57.50
β-D-ribo	**10**β	108.31	74.57	71.16	83.20	63.16	55.50
α-L-arabino	**8**α	108.64	81.04[a]	76.68	84.22[a]	61.54	55.24
β-L-arabino	**8**β	102.49	76.65	74.82	82.30	63.42	55.43
α-D-lyxo		108.48	76.33	71.37	80.71	60.50	56.26

[a] Assignment not unequivocal.

Table 5 ^{1}H NMR Data [400 MHz, $CDCl_3$/TMS, δ (ppm), *J* (Hz)] of Methyl 2,3-Anhydro-aldopentofuranosides

Furanoside	Nr.	1-H	2-H	3-H	4-H	5-H	5'-H	OMe	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
α-D-ribo[a]	**1**α	5.21	3.80	3.74	4.32	3.67	3.71	3.51	0.7	2.9	0	3.6	3.6	11.5
β-D-ribo	**1**β	4.97	3.78[d]	3.71[d]	4.27	3.67	3.72	3.47	0	2.7	0	3.4	3.4	12.3
α-D-lyxo	**4**α	4.97	3.66	3.76	4.13	3.86	3.86	3.43	0	2.9	0.6	5.3	5.3	–
α-L-lyxo[c]	**9**α	4.97	3.66	3.76	4.13	3.85	3.85	3.43	0	2.9	0.5	5.3	5.3	–
β-D-lyxo[b]	**4**β	5.01	3.71	3.73	4.03	3.86	3.90	3.53	0.6	3.0	0.9	5.5	5.6	11.3

[a] Only prepared according to lit.[1]
[b] Only prepared according to lit.[3]
[c] Only prepared by Mitsunobu reaction, this paper.
[d] Assignment not unequivocal.

Table 6 ^{13}C NMR Data [101 MHz, $CDCl_3$/TMS, δ (ppm)] of Methyl 2,3-Anhydro-aldopentofuranosides

Furanoside	Nr.	1-C	2-C	3-C	4-C	5-C	OMe
α-D-ribo[a]	**1**α	102.76	56.35	57.57	78.82	62.90	57.57
β-D-ribo	**1**β	102.26	55.07[d]	56.21[d]	79.59	62.78	55.96
α-D-lyxo	**4**α	102.23	55.86	54.10	76.36	61.65	55.61
α-L-lyxo[c]	**9**α	102.22	55.85	54.09	76.38	61.59	55.60
β-D-lyxo[b]	**4**β	102.45	55.41	54.92	76.80	61.81	56.94

[a] Only prepared according to lit.[1]
[b] Only prepared according to lit.[3]
[c] Only prepared by Mitsunobu reaction, this paper.
[d] Assignment not unequivocal.

Diastereomeric Mixture

EI MS: *m/z* (%) 208 (2, M^+−O-CH-OCH_3), 179 (9), 155 (2), 144 (2), 121 (4), 115 (2), 101 (9), 87 (6), 85 (9), 84 (7), 73 (8), 59 (7), 45 (31), 43 (100, CO-CH_3).

FAB MS (*m*-NBA): *m/z* (%) 269 (M^++1).

Anal. Calcd for $C_8H_{12}O_6S_2$: C, 35.81; H, 4.51; S, 23.90. Found: C, 35.93; H, 4.42; S 23.98.

***endo*-12β:**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, SAc), 3.08 (dd, 1H, H-5), 3.24 (dd, 1H, H-5'), 3.43 (s, 3H, OMe), 4.57 (ddd, 1H, H-4), 5.11 (dd, 1H, H-3), 5.13 (d, 1H, H-2), 5.30 (s, 1H, H-1). $J_{1,2}$ = 0, $J_{2,3}$ = 6.6, $J_{3,4}$ = 0.9, $J_{4,5}$ = 6.7, $J_{4,5'}$ = 8.8, $J_{5,5'}$ = 13.9 Hz.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.57 (SAc), 32.39 (C-5), 55.47 (OMe), 85.29 (C-4), 89.54, 91.02, 108.78 (C-1), 194.66 (C=O).

***exo*-12β:**

$[\alpha]_D^{20}$ −60.8° (*c* 1.0, $CHCl_3$).

IR (KBr): ν = 3005, 2993, 2957, 2943, 2914, 2839 (C-H), 1691 (C=O), 1207 (S=O), 1145, 1107, 1068, 1039 (C-O), 690 (S-O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, SAc), 3.11 (dd, 1H, H-5), 3.22 (dd, 1H, H-5'), 3.41 (s, 3H, OMe), 4.31 (ddd, 1H, H-4),

5.08 (s, 1H, H-1), 5.33 (d, 1H, H-2 or H-3), 5.35 (d, 1H, H-2 or H-3). $J_{1,2}$ = 0, $J_{2,3}$ = 6.2, $J_{3,4}$ = 0.4, $J_{4,5}$ = 6.8, $J_{4,5'}$ = 9.0, $J_{5,5'}$ = 13.9 Hz.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.57 (SAc), 32.05 (C-5), 55.40 (OMe), 84.58 (C-4), 86.69 (C-3), 87.85 (C-2), 108.34 (C-1), 194.45 (C=O).

HR FAB MS (*m*-NBA) [M^++H]: calcd 269.0154. Found: 269.0102 (M^++1).

Anal. Calcd for $C_8H_{12}O_6S_2$: C, 35.81; H, 4.51; S, 23.90. Found: C, 35.84; H, 4.44; S 24.10.

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