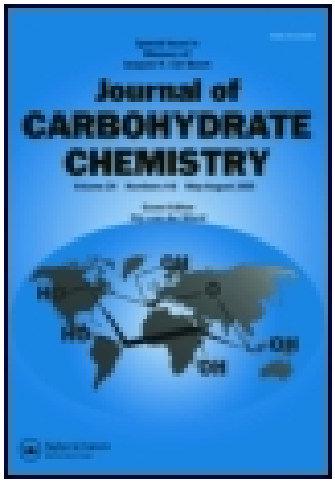

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Methyl 5-Deoxy-α and β-D-Xylofuranosides

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METHYL 5-DEOXY-α AND β-D-XYLOFURANOSIDES

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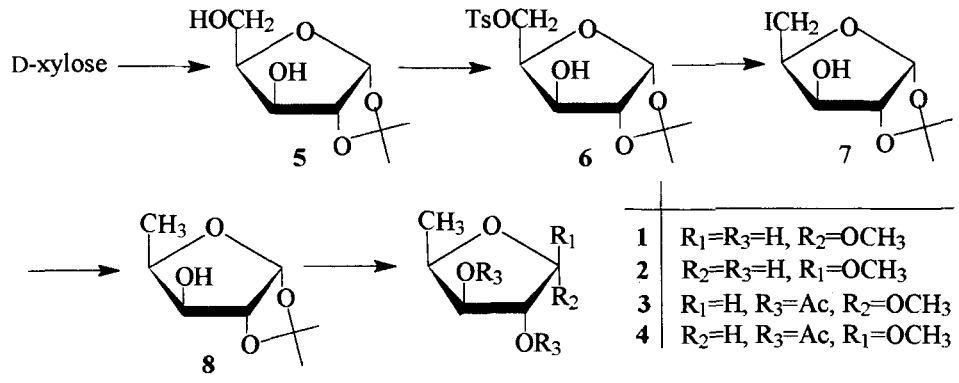
ABSTRACT

Synthesized from D-xylose, methyl 5-deoxy-α-D-xylofuranoside (**1**) and methyl 5-deoxy-β-D-xylofuranoside (**2**) were obtained in overall yields of 24 and 26 %, respectively. The key step in the synthesis was the separation of an anomeric mixture on a strong anion exchanger in OH^- form. NMR data and mass spectra of title compounds **1**, **2**, methyl 2,3-di-*O*-acetyl-5-deoxy-α-D-xylofuranoside (**3**), and methyl 2,3-di-*O*-acetyl-5-deoxy-β-D-xylofuranoside (**4**) are discussed. The conformations of **1** and **2** were established from the best fit between calculated and experimental coupling constants using Karplus equation.

INTRODUCTION

As we decided to study the stereochemistry and biological activity of 5-deoxy pentose derivatives, we needed a large quantity of both methyl 5-deoxy-α-D-xylofuranoside (**1**) and methyl 5-deoxy-β-D-xylofuranoside (**2**). The preparation of **1** has



Scheme 1

been described previously by an eight step procedure[1] from D-xylose *via* methyl 3,5-*O*-isopropylidene-α-D-xylofuranose with an overall yield of ca. 6 %. Compound **2** was identified only by mass spectroscopy[2] as a by-product in a reaction of methyl 2,3-di-*O*-benzylidene-5-*O*-benzoyl-β-D-ribofuranoside with *N*-bromosuccinimide.[3] 1,2-*O*-Isopropylidene-α-D-xylofuranose (**5**) seemed to be a suitable starting material for the synthesis of **1** and **2**, because it can be quickly and easily synthesized[4] and converted[5] to an anomeric mixture of the target compounds. A serious drawback of this method has been unsuccessful separation of **1** and **2** by silica gel chromatography.[6]

RESULTS AND DISCUSSION

Using the described reaction pathway from **5** to **8** (Scheme 1), but changing the experimental conditions and using the crude intermediates before the final purification, we improved an overall yield of **8** and decreased all reaction times. Compound **6** was obtained by treatment of solid *p*-toluenesulfonyl chloride (2.0 molar excess) on crude **5** (product of a one-pot synthesis[4]) in pyridine at ambient temperature. Tosylation was completed in a few minutes and 96 % of **6** was precipitated by direct dilution with water.[7] The yield of **6**, contaminated with about 5 % of di-*O*-tosyl derivative, was 84 % based on D-xylose in

comparison with 61 % (based on **5**) from the classical procedure[8] requiring a tedious extraction and more than 24 hours. The conversion of **6** to **7** was achieved with sodium iodide in 2-butanone[9] in 12 h and, finally, hydrogenation of **7** with Raney nickel in the presence of triethylamine[10] afforded, after crystallization, **8** in 48 % yield, calculated from D-xylose.

The methanolysis of **8** to **1** and **2**, carried out using a cation exchanger in H^+ form and methanol at 80 °C, was monitored by GLC and an optimized reaction time was established to be 120 min. Under these conditions, a ratio of **2/1** = 1.2 was found, similar to 1.0 published from NMR data of an anomeric mixture[5] of **1** and **2**. Chromatography on strong anion exchanger in OH^- form with water as an eluent afforded successively crystalline **1**, and **2** as a syrup in yields of 42 % and 51 %, respectively. Acetylation of **1** and **2** with acetic anhydride in pyridine led to the di-*O*-acetyl derivatives **3** and **4**.

Mass spectra. Mass spectra of **1** and **2**, obtained by electron impact ionization, are identical within experimental error (Table 1). No molecular-ion peak was found and both **1** and **2** spectra exhibited a peak at *m/z* 117 for the loss of the C1 methoxyl group. A peak at *m/z* 116 corresponding to the loss of methanol is visible only in the spectrum of **2**. This fragmentation was previously observed for methyl xylofuranosides.[11] A significant peak at *m/z* 73 in the spectra of **1** and **2** was attributed[2] previously to the loss of a methyl radical from the ion at *m/z* 88 making it characteristic of the 5-deoxy furanoid structure.[2] Loss of C1 methoxyl group from the molecular-ions of diacetates **3** and **4** gave *m/z* 201, and *m/z* 188 can be explained by C5-C4-O4 fragmentation of acetaldehyde in analogy to the fragmentation of methyl ethers of furanosides.[12] The series of ions at *m/z* 172→129→87 is initiated by loss of methyl formate. The mass spectra of **3** and **4** are identical and thus not useful for a resolution of the anomers, but the fragmentation of acetaldehyde and methyl formate from the molecular-ion can be used as an evidence for the 5-deoxy furanoid structure.

NMR. The ^{1}H NMR data from **1** and **2** (Table 2) are in agreement with proton signal assignments previously described for both **1**[1] and an anomeric mixture.[5,13] However, one exception can be observed in the values of $J_{1,2}$, which are reversed in reference 5. The H1 and H2 chemical shifts are the same as for methyl α(β)-D-xylofuranoside,[14] but

Table 1. Mass spectra of compounds **1** and **2**

m/z	Relative abundance		*m/z*	Relative abundance	
	1	**2**		**1**	**2**
117	8.6	7.0	69	25.0	23.7
116	—	2.8	68	5.7	6.5
104	2.4	0.9	61	33.8	29.5
103	3.0	1.9	60	5.0	8.6
99	4.2	2.4	59	7.7	7.3
98	1.2	0.7	58	21.5	16.5
88	37.1	40.1	57	57.7	56.0
87	27.8	28.6	56	3.7	4.0
86	27.1	25.7	55	14.3	14.3
85	32.8	30.1	54	7.1	10.2
77	5.6	4.3	53	3.5	3.2
74	11.5	6.8	44	5.0	8.6
73	63.7	60.8	45	32.8	39.8
72	22.6	20.0	43	21.5	26.5
71	22.6	25.8	42	22.6	24.6
70	100.0	100.0	41	23.8	26.6

Table 2. ^{1}H NMR Data of **1** and **2** in $CDCl_3$[a] and D_2O[b]: chemical shifts δ [ppm]; (J [Hz])

Compound	H-1	H-2	H-3	H-4	H-5	CH_3O	2-OH	3-OH
	($J_{1,2}$)	($J_{2,3}$)	($J_{3,4}$)	($J_{4,5}$)	—	—	($J_{2,OH}$)	($J_{3,OH}$)
1[a]	4.96	4.09	4.06	4.31	1.24	3.48	3.00	2.47
	(4.4)	(3.6)	(4.6)	(6.5)	—	—	—	—
1[b]	5.00	4.13	4.11	4.38	1.21	3.45	—	—
	(4.2)	(4.3)	(4.9)	(6.6)	—	—	—	—
2[a]	4.78	4.15	3.87	4.44	1.31	3.38	3.93	3.18
	(~0)	(~0)	(4.3)	(6.6)	—	—	(3.2)	(10.3)
2[b]	4.83	4.11	4.01	4.44	1.28	3.39	—	—
	(~0)	(1.6)	(4.4)	(6.6)	—	—	—	—

Table 3. ^{13}C NMR Data of methyl glycofuranosides in $CDCl_3$: chemical shifts δ [ppm]

Methyl furanoside	C-1	C-2	C-3	C-4	C-5	CH_3O
β-L-threoside[a]	103.8	77.4	75.8	72.0	—	56.2
5-deoxy-α-D-xylofuranoside (**1**)	101.5	78.8	77.6	74.9	14.3	55.8
α-D-xylofuranoside[a]	103.0	77.8	76.2	79.3	61.6	56.7
α-L-threoside[a]	109.4	80.5	76.2	73.2	—	55.2
5-deoxy-β-D-xylofuranoside (**2**)	108.5	80.2	77.1	78.9	15.3	55.0
β-D-xylofuranoside[a]	109.7	81.0	76.0	83.6	62.2	56.4

a. Reference 16

replacement of hydroxymethyl group by methyl at C4 results in a downfield shift of H4 (0.1 ppm) and upfield shifts of H3 (0.2 ppm) and H5 (2.5 ppm), respectively. The configuration of C1 in **1** and **2** was easily derived from the $J_{1,2}$ coupling (Table 2), which is nearly zero for H1-H2 *trans* orientation[13] in **2**. This conclusion is confirmed also from the ^1H NMR of corresponding diacetates **3** and **4** (see Experimental). The assignment of the anomeric configurations of **1** and **2** was also made using the well established rule[15] relating C1 chemical shift to the relative orientation of O1 and O2: furanose anomers having O1 and O2 *cis* give a C1 signal upfield to the corresponding anomer having these atoms *trans* (Table 3, for **3** and **4** see Experimental). The substitution at C4 (threoside → 5-deoxyxylofuranoside → xylofuranoside) is connected with changes of the chemical shifts of C4 and C5 atoms (Table 3), and the largest effect occurs, as expected, at C5. The downfield shift of C4 (3.0 ppm for **1**, 6.0 ppm for **2**) is remarkable.

Conformations. Conformational analysis of the 5-membered furanose ring utilizes the concept of pseudorotation[17] with two quantitative descriptors[18] — the puckering amplitude (Φ_m) and the phase angle of pseudorotation (P). However, assigning solution conformations to the title derivatives from NMR data is a challenging problem due to the substantial flexibility of the furanose ring. Small free-energy differences between the various twist (T) and envelope (E) ring conformers result in a range of conformers for a furanose sugar.[19] As conformational interconversions are very fast at room temperature

compared to the NMR time-scale, NMR data can only give information about time-averaged conformations. Unfortunately, it is very difficult to deduce from NMR data, whether these represent a single conformer, a range of conformations or even two separate regions. For this reason we evaluated both a one-state and a two-state conformational model, calculated their NMR couplings, and compared them with experimental ones. As this modeling involved some guess-work in fitting to experimental values, all conformations thus deduced are rationalized against the general rules for preferred furanose.[20] As the methyl group at C-4 is less bulky than the hydroxymethyl group in regular xylofuranose derivatives, it may be expected that the conformers will be less sensitive to the position of the exocyclic group at C-4.

For the translation of vicinal ^{1}H NMR coupling constants ($^3J_{HH}$) into proton-proton torsion angles (ϕ) an empirical generalization[21] of the classical Karplus equation was used throughout this paper (Equation 1). It should be noted, that even this latest form of the Karplus equation does not reproduce accurate $^3J_{1,2}$ couplings around ϕ = 90°, where the experimental values are often up to 1 Hz smaller than the minimum of the function.[22]

$$^3J_{HH} = P_1 \cos^2\phi + P_2 \cos\phi + P_3 + \sum \Delta\chi_i \left\{ P_4 + P_5 \cos^2\left(\xi\phi + P_6 |\Delta\chi_i|\right)\right\} \quad (1)$$

Interrelation between proton-proton torsion angles $\phi_{i,j}$ and endocyclic carbon-carbon or carbon-oxygen torsion angles was expressed as a direct dependence on pseudorotation parameters P and Φ_m according to Altona *et al.*[23]

α-D-xylose

$$\phi_{1,2} = 3{,}3° + 1.102\,\Phi_m \cos(P - 144°)$$
$$\phi_{2,3} = -119.8° + 1.090\,\Phi_m \cos P \quad (2)$$
$$\phi_{3,4} = -4{,}9° + 1.095\,\Phi_m \cos(P + 144°)$$

β-D-xylose

$$\phi_{1,2} = 123.3° + 1.102\,\Phi_m \cos(P - 144°) \quad (3)$$

One-State Model Calculations. With P values in the range of <9°; 18°....360°> (40 values) and Φ_m values in the range of <15°; 18°....45°> (11 values) all coupling

Table 4. Best-fit values[a] for a one-state model

Compound	P [°]	Φ_m [°]	$\Delta J_{1,2}$	$\Delta J_{2,3}$	$\Delta J_{3,4}$	RMS [Hz]
1[b]	108	42	0.29	0.12	0.82	0.51
1[c]	108	42	0.79	-0.17	0.52	0.55
2[b]	0	27	0.51	0.11	-0.04	0.30
2[c]	−18	36	0.65	-0.41	-0.04	0.44

a. Coupling constants are measured with 0.1 Hz accuracy (Table 2), deviations between *theoretical* and *experimental* are given up to 0.01 Hz; b. $CDCl_3$; c. D_2O

constants were calculated using equations (1) – (3) and compared with experimental values (Table 4).

Two-State Model Calculations. For a two-state model, an equilibrium N-conformer ⇔ S-conformer is assumed,[24] where the experimental NMR coupling constants are weighted averages of coupling constants of the conformers present, and is given by Equation 4. With three observable ring coupling constants it is not possible to solve this

$$J_{exp} = x_N J_N + (1 - x_N) J_S \tag{4}$$

problem analytically and, as in the previous case, calculated theoretical coupling constants were fitted to the experimental values.

Thus, for P_N in the range of <–81°; –72°....+90°>, P_S in the range of <99°; 108°....270°>, Φ_N and Φ_S, respectively, as in the previous case, and x_N within <0; 0.1....1>, all N/S conformational equilibria were modeled, and, using equations (1) – (4), all coupling constants were calculated (Table 5).

For α-anomer **1**, the above mentioned conformational criteria cannot be fully satisfied all at once. Therefore, there is no single preferred conformation. Relatively high difference in RMS values between a one-state model and a two-state one suggest that the latter is more probable both in $CDCl_3$ and D_2O. Calculated NMR couplings of an approximately 1:1 mixture of $^3T_2$ and E_1 or ^2E conformers in $CDCl_3$ and $^3T_2$ and ^2E conformers in D_2O agree very well with experimental values. Stevens[25] found a $^0T_1$ or $^2T_3$

Table 5. Best-fit values for a two-state model

Compd.	P_N [°]	Φ_N [°]	P_S [°]	Φ_S [°]	x_N	$\Delta J_{1,2}$	$\Delta J_{2,3}$	$\Delta J_{3,4}$	RMS [Hz]
1[a]	9	39	126	36	0.5	–0.02	0.03	0.00	0.02
1[b]	–9	42	162	27	0.6	0.05	–0.01	–0.01	0.03
2[a]	9	30	270	42	0.8	0.52	0.41	0.05	0.38
2[b]	18	36	261	42	0.6	0.55	0.03	0.03	0.32

a. $CDCl_3$; b. D_2O

conformation for α-xylofuranose esters in $CDCl_3$, while Angyal[20] reports $^2T_3$ or $^3T_2$ conformations for methyl α-D-xylofuranoside in D_2O. For β-anomer **2**, both models yield the E_2 - ^3E range as the major conformer, which is in agreement with published data.[20,25] The RMS values do not exclude any model. However, relatively high puckering amplitudes calculated for the minor E_0 conformers in a two-state model seem to be less probable. Furthermore, for this configuration, where the methoxyl group at C-1 and the methyl group at C-4 are *cis*-oriented, a single conformation may be expected, because all three criteria are satisfied by the $^3T_2$ or $^2T_3$ conformation. Therefore we assume that the β-anomer **2** adopts the $^3T_2$ conformation in $CDCl_3$ and the E_2 conformation in D_2O. Literature data state $^3T_2$ or E_3 for β-xylofuranose esters in $CDCl_3$[25] and $^3T_2$ for methyl-β-D-xylofuranoside in D_2O.[20]

EXPERIMENTAL

General procedures. Optical rotations were measured on an Opton Photoelectric Precision Polarimeter 0.005. Melting points were determined with a Kofler hot block and are uncorrected. NMR data were extracted from spectra measured in solutions of $CDCl_3$ (with TMS as an internal standard) or D_2O at 25 °C with a BRUKER AM-400 spectrometer. ^{13}C NMR assignments were made using a HETCOR experiment and ^1H

NMR shifts were obtained by first order analysis of the spectra using a COSY experiment and from selective decoupling. Mass spectra were recorded on a JEOL DX 303 instrument using an EI technique at 70 eV. Anion exchange chromatography was carried out on a strong anion exchanger DOWEX 1x2 (200-400 mesh, Cl^- form, Fluka) after transformation into the OH^- form at 25 °C with water as a mobile phase. Column chromatography was performed on Silica Gel Lachema (Brno, Czech Republic), 100-160 μm, and TLC on Silica Gel G according to Stahl, 10-40 μm (Merck, Darmstadt). Compounds on TLC plates were visualized by spraying with 1% cerium(IV)sulfate in 10 % sulfuric acid and subsequent mineralization. Solutions were concentrated under reduced pressure with a bath temperature below 40 °C.

GLC. GLC was performed with a Hewlett-Packard 5890 A instrument equipped with a flame-ionization detector. A fused silica capillary column (50 m x 0.31 mm I.D.) with chemically bonded phenyl methyl silicone (5 %, film thickness 0.5 μm) was used with nitrogen as a carrier gas at a flow rate 8.1 mL min^{-1}. Oven temperature was programmed (100→160 °C, 4 °C min^{-1}), detector at 230 °C and injector at 200 °C. The following retention times (in min) were obtained: **1**, 8.36; **2**, 9.23; **3**, 17.08; **4**, 17.53; **8**, 11.03.

HPLC. A glass jacketed column (25 cm x 6 mm I.D.) containing a strong cation exchanger OSTION LGKS 0802 (H^+ form, Spolek pro chemickou a hutní výrobu, Ústí nad Labem, Czech Republic) in Na^+ form thermostated at 53 °C was used. The flow rate of deionized water was maintaned at 6 mL h^{-1} with a Beckman 100 A pump and analyses were monitored with an IR detector Optilab 5902 (Tecator, Sweden) connected to a recorder TZ 4200 (Laboratorní přístroje, Czech Republic). The following capacity factors were obtained: **1**, 1.45; **2**, 1.30; **8**, 1.85.

1,2-*O*-Isopropylidene-5-*O*-(*p*-toluenesulfonyl)-α-D-xylofuranose (6). To a stirred solution of crude **5** (13.8 g, prepared from 10 g of D-xylose)[4] in dry pyridine (56 mL) was added solid *p*-toluenesulfonyl chloride at ambient temperature (usually 32.5 g, 2.5 mol) until the starting **5** was gone, TLC (benzene-acetone 8:1). The mixture was then diluted with water (500 mL), a solid **6** was filtered off and washed with water (500 mL). The crude **6** (19.4 g, 84 % yield based on D-xylose), mp 128-130 °C, mp 133-134 °C,[26] was used without any purification in the next step.

5-Deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose (7). The crude **6** (19.4 g) was stirred in 2-butanone (160 mL) with sodium iodide (76 g) at 110 °C under reflux and monitored by TLC (benzene-acetone 8:2). After 12 h, the solvent was evaporated and a solid residue extracted between water and chloroform. A chloroform layer was washed with sodium thiosulfate and sodium hydrogencarbonate solutions, and finally with water, dried over magnesium sulfate and the solvent evaporated to give a crude crystalline **7** (16.7 g), mp 98-101 °C , mp 108-109 °C,[26] mp 109-110 °C.[27]

5-Deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (8). The crude **7** (16.7 g) in methanol (300 mL) and triethylamine (7 g) was hydrogenated in the presence of Raney nickel. After 48 h, the mixture was filtered through Celite, concentrated to dryness and mixed with diethyl ether. Undissolved salts were filtered off and extracted with diethyl ether. After solvent evaporation, the crude **8** (6.6 g) was obtained, mp 58-62 °C, which gave after crystallization (diethyl ether-petroleum ether, 40-60 °C) 5.6 g of **8** (48 % yield based on starting D-xylose), mp 65-66 °C, mp 68-69 °C.[28] MS and NMR results were in agreement with previous findings.[28]

Methanolysis of 5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (8). Compound **8** (400 mg, 2.6 mmol) was heated in methanol (10 mL) with DOWEX 50 Wx8 (H^+ form, 1 mL, saturated with methanol) under reflux at 80 °C during 4 h. The aliquots (0.5 mL) were filtered, 0.1 mL of filtrate was added to methanol (0.2 mL) and 0.5 μL of this clear solution was analyzed by GLC. An optimized reaction time was 120 min.

Methyl 5-deoxy-α-D-xylofuranoside (1). Methyl 5-deoxy-β-D-xylofuranoside (2). Compound **8** (1.0 g, 6.5 mmol) was stirred in methanol (25 mL) with a strong cation exchange resin (H^+ form, 2.5 mL) at 80 °C as described above. After 120 min, the resin was filtered off, washed with methanol and combined filtrates were concentrated to yield 0.8 g (94 %) of a semisolid anomeric mixture with **2** slightly prevailing (**2/1** =1.2, by GLC). The mixture was diluted with water (5 mL) and separated on a strong anion exchanger (DOWEX 1x2 in OH^- form, 70 mL, water). The initial volume (80 mL) was discharged and following fractions (5 mL) were then combined according to HPLC analysis. First eluted was α-anomer **1** (360 mg, 45 %), an overall yield 24 %, $[\alpha]_D^{21}$

+141.3° (*c* 0.9, $CHCl_3$), mp 83-84 °C, $[\alpha]_D^{24}$ +149.1° (*c* 1.0, $CHCl_3$),[1] mp 83-85 °C.[1] NMR and MS data are given in Table 1 - 3.

Anal. Calcd for $C_6H_{12}O_4$: C, 48.65; H, 8.11. Found: C, 48.56; H, 8.05.

The β-anomer **2** (430 mg, 55 %) was a syrup at ambient temperature, but crystallized at -70 °C from ethyl acetate on standing, $[\alpha]_D^{24}$ -99.8° (*c* 1.9, water). NMR and MS data are sumarized in Table 1 - 3.

Anal. Calcd for $C_6H_{12}O_4$: C, 48.65; H, 8.11. Found: C, 48.50; H, 8.02.

Methyl 2,3-di-*O*-acetyl-5-deoxy-α-D-xylofuranoside (3). To a solution of **1** (100 mg, 0.68 mmol) in pyridine (1.7 mL) was added acetic anhydride (1.7 mL, 15.4 mmol) at ambient temperature. After the reaction was complete (TLC, toluene - ethanol 20 : 1), water was added, the mixture concentrated to dryness and separated by flash chromatography on silica gel (30 g, toluene - ethanol 20 : 1) to yield **3** (140 mg, 89 %) as a syrup: $[\alpha]_D^{22}$ +169.5° (*c* 1.6, $CHCl_3$). ^1H NMR ($CDCl_3$) δ [ppm]: 1.18 (d, 3H, $J_{4,5}$ 6.5 Hz, H-5), 2.14 (s, 6H, 2 x CH_3CO), 3.38 (s, 3H, CH_3O), 4.42 (m, 1H, $J_{3,4}$ 5.9 Hz, $J_{4,5}$ 6.5 Hz, H-4), 4.99 (dd, 1H, $J_{1,2}$ 4.6 Hz, $J_{2,3}$ 4.6 Hz, H-2), 5.08 (d, 1H, $J_{1,2}$ 4.6 Hz, H-1), 5.37 (dd, 1H, $J_{2,3}$ 4.6 Hz, $J_{3,4}$ 5.9 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ [ppm]: 170.2 (CO), 99.9 (C-1), 78.1 (C-2), 76.5 (C-3), 72.6 (C-4), 55.3 (CH_3O), 20.6 (CH_3CO), 14.4 (C-5); MS (*m/z*) 202 (0.2), 201 (1.7), 188 (0.9), 172 (0.4), 130 (14.0), 129 (11.1), 99 (9.9), 88 (9.3), 87 (30.3), 69 (11.4), 43 (100.0).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.90. Found: C, 51.80; H, 6.85.

Methyl 2,3-di-*O*-acetyl-β-D-xylofuranoside (4). Compound **2** was acetylated as described above and **4** was isolated as a syrup (136 mg, 87 %): $[\alpha]_D^{23}$ -22.2° (*c* 1.6, $CHCl_3$); ^1H NMR ($CDCl_3$) δ [ppm]: 1.25 (d, 3H, $J_{4,5}$ 6.6 Hz, H-5), 2.10 (s, 3H, CH_3CO), 2.14 (s, 3H, CH_3CO), 3.42 (s, 3H, CH_3O), 4.51 (m, 1H, $J_{3,4}$ 5.5 Hz, $J_{4,5}$ 6.6 Hz, H-4), 4.83 (s, 1H, $J_{1,2}$ ~0 Hz, H-1), 5.10 (s, 1H, $J_{1,2}$ ~0 Hz, $J_{2,3}$ ~0 Hz, H-2), 5.18 (dd, 1H, $J_{2,3}$ 1.4 Hz, $J_{3,4}$ 5.5 Hz, H-3); ^{13}C NMR ($CDCl_3$) δ [ppm]: 170.2 (CO), 169.6 (CO), 107.0 (C-1), 81.5 (C-2), 77.1 (C-4), 76.4 (C-3), 55.5 (CH_3O), 20.8 (CH_3CO), 20.7 (CH_3CO), 15.7 (C-5); MS (*m/z*) 201 (1.7), 188 (0.9), 172 (1.1), 130 (19.3), 129 (12.6), 99 (8.9), 88 (11.1), 87 (16.1), 85 (24.3), 69 (12.7), 43 (100.0). Reference 29, ^1H NMR ($CDCl_3$) δ [ppm]: 1.22 (d, $J_{4,5}$ 6 Hz), 2.06 (s, CH_3CO), 3.34 (s, CH_3O), 4.42 (bq, $J_{4,5}$ 4 Hz), 4.73 (s),

5.01 (s), 5.07 (dq) contamined with minor **3**:1.14 (d, $J_{4,5}$ 6 Hz), 3.32 (s, CH_3O), 5.15 - 5.39 (m).

Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.72; H, 6.90. Found: C, 51.81; H, 6.82.

REFERENCES AND NOTES

1. K. J. Ryan, H. Arzoumanian, E. M. Acton and L. Goodman, *J. Am. Chem. Soc.*, **86**, 2497 (1964).
2. D. C. DeJongh, J. D. Hribar and S. Hanessian, *Adv. Chem. Ser.*, **74**, 202 (1968).
3. S. Hanessian and N. R. Plessas, *J. Org. Chem.*, **34**, 1053 (1969).
4. J. Moravcová, J. Čapková and J. Staněk, *Carbohydr. Res.*, **263**, 61 (1994).
5. B. Green and H. Rembolt, *Chem. Ber.*, **99**, 2162 (1966).
6. Separation of 3-*O*-methanesulfonyl- (K. Hiroyshi and E. Sakae, *Agr. Biol. Chem.*, **27**, 689 (1963).) and 3-*O*-(*p*-toluenesulfonyl)- (H. Yamamoto, H. Sasaki and S. Inokawa, *Carbohydr. Res.*, **100**, C44-C45 (1982); *ibid.*, **132**, 287 (1984).) derivatives of **1** and **2** on silica gel are only described. Di-*O*-acetyl derivatives **3** and **4** were not separable.[29]
7. Remaining 4 % of **6** together with about 3 % of di-*O*-(*p*-toluenesulfonyl) derivative was chromatographically isolated from a chloroform extract of mother liquour.
8. R. S. Tipson, *Methods Carbohydr. Chem.*, **2**, 248 (1964).
9. V. K. Srivastava and L. M. Lerner, *J. Med. Chem.*, **22**, 24 (1979).
10. H. M. Kissman and R. Baker, *J. Am. Chem. Soc.*, **79**, 5534 (1957).
11. V. Kovacik and P. Kovac, *Carbohydr. Res.*, **24**, 23 (1972).
12. K. Heyns and H. Scharmann, *Tetrahedron*, **21**, 507 (1965).
13. E. J. Reist, V. J. Bartuska, D. F. Calkins and L. Goodman, *J. Org. Chem.*, **30**, 3401 (1965).
14. A. S. Serianni and R. Baker, *J. Org. Chem.*, **49**, 3292 (1984).
15. J. R. Snyder and A. S. Serianni, *Carbohydr. Res.*, **163**, 169 (1987).
16. R. G. S. Ritchie, N. Cyr, B. Korsch, H. J. Koch and A. S. Perlin, *Can. J. Chem.*, **53**, (1975).
17. J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).
18. C. Altona and M. Sundaralingam, *J. Am. Chem. Soc.*, **94**, 8205 (1972).
19. J. F. Stoddart in *Stereochemistry of Carbohydrates*, Wiley-Interscience, New York, 1971, pp 97-102.
20. S. J. Angyal, *Carbohydr. Res.*, **77**, 37 (1979).
21. C. A. G. Haasnoot, F. A. A. M. de Leeuw and C. Altona, *Tetrahedron*, **36**, 2783 (1980).
22. J. Staněk, Jr., J. Moravcová and J. Jarý, *J. Carbohydr. Chem.*, **4**, 79 (1985); I. Raich: PhD. Thesis, Prague, 1994.
23. F. A. A. M. de Leeuw and C. Altona, *J. Chem. Soc. Perkin Trans. 2*, **1982**, 375.
24. This type of conformational equillibria, with barriers at ^0E and E_0, resp. (P = 90° and P = 270°, resp.), is most commonly observed for furanose derivatives.

25. J. D. Stevens and H. G. Fletcher, *J. Org. Chem.*, **33**, 1799 (1968).
26. R. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **102**, 317 (1933).
27. R. A. Levene and J. Compton, *J. Biol. Chem.*, **111**, 325 (1935).
28. J. M. J. Tronchet and R. Graf, *Helv. Chim. Acta*, **55**, 1141 (1972).
29. D. H. Hollenberg, K. A. Watanabe and J. J. Fox, *Carbohydr. Res.*, **42**, 241 (1975).