Stereoselective β-*C*- and β-*S*-Glycosylation of 2-Deoxyribofuranose Derivatives Controlled by the 3-Hydroxy Protective Group

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(Received September 29, 1988)

β-*C*-2-Deoxyribofuranosides and β-*S*-2-deoxyribofuranosides are prepared stereoselectively from 1-*O*-acetyl-5-*O*-benzyl-3-*O*-[2-(methylsulfinyl)ethyl]-2-deoxy-D-*erythro*-pentofuranose or the corresponding 3-*O*-(2-pyridylmethyl)pentofuranose *N*-oxide by the reaction with silyl enol ethers or trimethlsilyl sulfides in the presence of a Lewis acid.

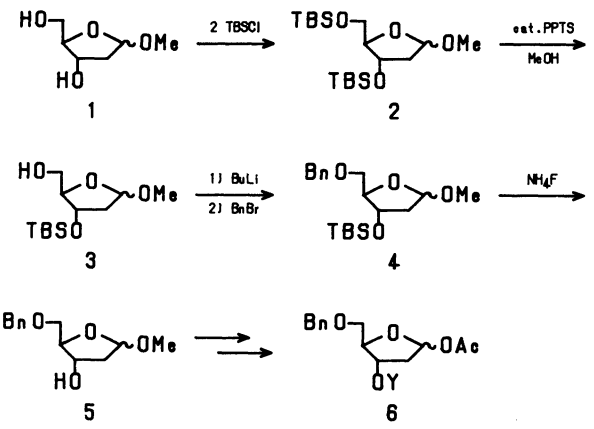
Because of the potential utility in chemotherapeutic studies and in biochemical investigation of specific enzyme-catalyzed reactions, much effort has been devoted to preparing various types of glycoside derivatives.[1] One of the problems in the synthesis of glycoside derivatives is the stereoselective formation of β-glycoside linkages.

In the synthesis of ribofuranosides and xylo-type furanosides which have 2-α-hydroxyl group, the formation of β-glycoside linkage is generally controlled by using neighboring group participation of the adjacent 2-α-*O*-acyl group (so called the Baker's 1,2-trans rule).[2] On the other hand, there is no generally applicable method to obtain β-isomers stereoselectively in the case of the preparation of glycosides which possess no 2-α-hydroxyl group such as 2-deoxy-, 2-fluoro-, and 2-arabino-type glycosides.[1-3] The exceptional high β-selectivity has been reported only in the S_N2 type displacement of 2-deoxy-α-D-*erythro*-pentofuranosyl halide by purine derivatives or cyanide under basic conditions[4] and by silylated pyrimidine[5] and 5-(acetyl)thiouracil[6] derivatives under the modified Hilbert-Johnson conditions.[5]

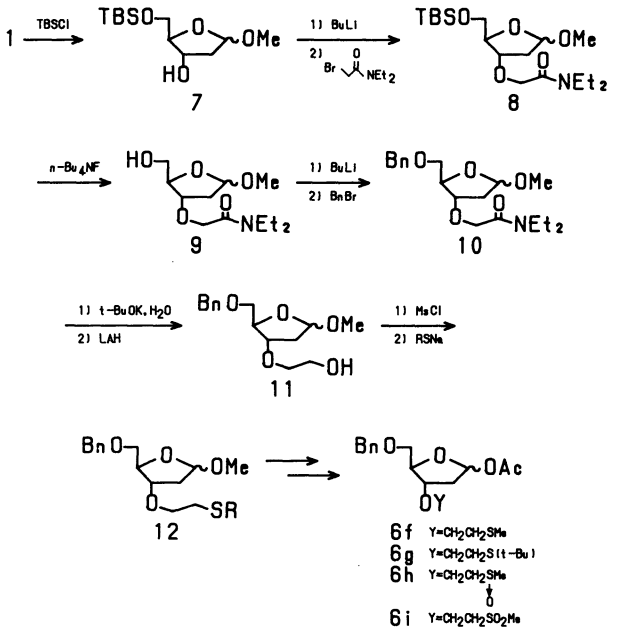
In this paper, we wish to report the results on the stereocontrol in glycosylation reaction by neighboring group participation of a 3-α-*O*-substituent of 2-deoxy-D-*erythro*-pentofuranose (2-deoxyribofuranose) derivatives.[7] It was considered that when a suitable 3-*O*-subtituent was introduced instead of an acyl group for stabilizing the 1-cationic center in acid catalyzed glycosylation reactions, the stereoselection of the glycosylation would be controlled to give β-glycosides selectively. We, therefore, investigated *C*-glycosylation of 2-deoxyribofuranose derivatives with silyl enol ethers in the presence of a Lewis acid employing 1-*O*-acetyl-5-*O*-benzyl-2-deoxyribofuranoses which have various substituents on the 3-hydroxyl group.

Various 3-*O*-substituted 2-deoxyribofuranoses such as 3-*O*-substituted 1-*O*-acetyl-5-*O*-benzyl-2-deoxyribofuranoses **6a—e** and 1-*O*-acetyl-5-*O*-benzyl-3-*O*-[2-(alkylthio)ethyl]-2-deoxyribofuranose **6f—i** are prepared from methyl 2-deoxy-D-ribofuranoside, and the synthetic pathways are outlined in Schemes 1 and 2, respectively.

In these courses of the synthses, alkylation reaction reaction of the 3- or 5-hydroxy intermediates containing a silyl protective group (**3** and **7**) met some troubles in the conventional reaction conditions (NaH/DMF),



Scheme 1.



Scheme 2.

because of the migration of the silyl group and a low yield of the desired alkylated product. However, the alkylation was found to proceed even at room temperature affording the alkylated products in excellent yield, when the lithium alkoxides of **3** and **7** generated by treatment with *n*-BuLi or *t*-BuOLi were treated with bromides in the presence of sodium iodide and hexamethylphosphoric triamide (HMPA) in tetrahydrofuran (THF). This procedure appears to be of general utility in alkylation of other hydroxy compounds **5** and **9**.

At first, the reaction of 3-*O*-benzyl derivative **6a** with 1-trimethylsilyloxy-1-phenylethylene **13a** was examined at −78 °C in dichloromethane in the presence of $SnCl_4$,[8] and the α-*C*-glycoside **14a** was found to be produced in good selectivity (α-**14a**:β-**14a**=82:18). This result means that the introduction of such a group like benzyl group which would not tightly interact with the 1-cationic center results in the highly preferential formation of the α-glycoside.

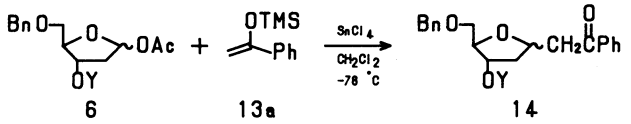
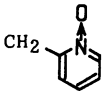


Table 1. Stereoselectivity of the Reaction of **6** and **13a**

6	Y	Yield of **14**/%	α : β
6a	CH_2Ph	92	82 : 18
6b	$CH_2OCH_2CH_2OMe$	83	75 : 25
6c	CH_2SMe	56	82 : 18
6d	$CH_2S(O)Me$	53	52 : 48
6e		87	49 : 51
6f	CH_2CH_2SMe	46	42 : 58
6g	$CH_2CH_2SBu^t$	44	68 : 32
6h	$CH_2CH_2S(O)Me$	92	32 : 68
6i	$CH_2CH_2SO_2Me$	54	50 : 50

In order to find out the suitable substituent for the selective preparation of the β-isomer, effects of the 3-*O*-substituents on the stereoselectivity were examined using various 3-*O*-derivatives and the results are listed in Table 1. Among a variety of 3-substituents such as ethers, esters, and sulfides, 2-(alkylthio)ethyl group was found to afford slight excess amounts of the β-isomer. That is, by employing **6f** which has 2-(methylthio)-ethyl group, the corresponding *C*-glycosides **14f** were obtained in 46% yield in the ratio of α:β=42:58.

It was also noted that the reaction in a solvent which has little donor ability[9] such as dichloromethane or toluene exhibited higher selectivity as compared with a solvent having large donar property (for example, α:β=89:11 in acetonitrile). The ratio of the α-isomer to the β-isomer was not influenced by the kind of Lewis acids, namely $SnCl_4$,[8] trityl perchlorate,[10] and trimethylsilyl trifluoromethanesulfonate (TMSOTf).[11]

Then, 2-(methylthio)ethyl derivative **6f** was converted to the corresponding sulfoxide **6h** by considering that the participation by the sulfinyl group should be more efficient with respect to the electronic and steric effects. The sulfoxide **6h** actually reacted with the silyl enol ether **13a**, giving the β-*C*-glycoside β-**14h** predominantly (α-**14h**:β-**14h**=32:68) in an excellent yield. Reaction of an analogous *N*-oxide derivative **6e** having 2-pyridylmethyl group *N*-oxide as a 3-*O*-functionality, however, afforded almost equal amount of α- and β-isomers.

As the introduction of 3-*O*-methylsulfinyl group revealed to realize a good β-selectivity, the reactions of

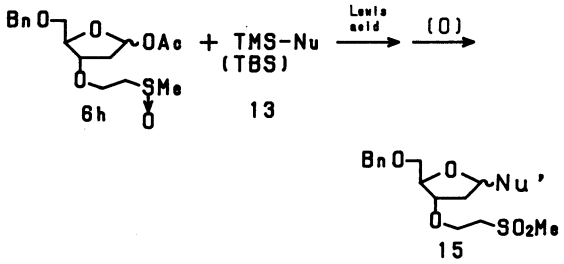
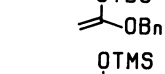
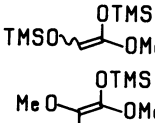
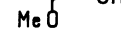
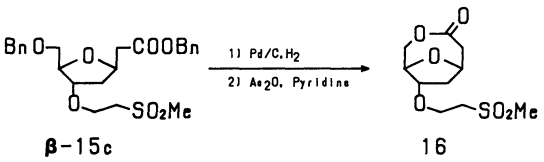


Table 2. Reaction of **6h** with Silyl Nucleophiles **13**

	Nucleophile	Lewis acid	**15**, Nu'	Yield **15**/%	α : β
13a		$SnCl_4$	CH_2COPh	92	32 : 68
13b		$SnCl_4$	CH_2COMe	82	22 : 78
13c		TMSOTf	CH_2COOCH_2Ph	86	9 : 91
13d		TMSOTf	CH(OH)COOMe	91	11 : 89
13e		TMSOTf	$C(OMe)_2COOMe$	73	33 : 67
13f		$SnCl_4$	$CH_2CH=CH_2$	50	87 : 13

6h with several silyl nucleophiles were examined using $SnCl_4$ or TMSOTf as a Lewis acid, and the results are summarized in Table 2.

The stereochemistry and the isomer ratio of these products are determined after conversion of the products to the corresponding sulfones **15**. The configuration of the major isomer of the *C*-glycosides **15c** was determined as the β-configuration by the transformation of **15c** into a lactone **16** by hydrogenolysis and successive treatment with acetic anhydride–pyridine.



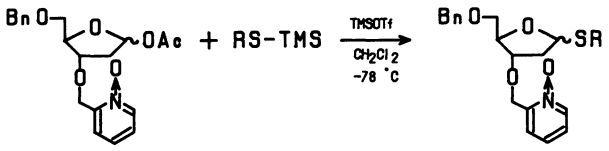
β-15c 16

Stereochemistry and isomer ratio of other products were determined by HPLC and by the comparison of their 400 MHz or 270 MHz ^1H NMR spectra with that of the above glycosides **15c**, in which the characteristic pattern of C-2 proton(s) appears as shown in Table 3.

The results in Table 2 clearly show that the stereoselectivity largely depends on the nucleophilicity of silyl nucleophiles. For example, allyltrimethylsilane, a weak nucleophile as compared with silyl enol ethers, affords the corresponding α-isomer predominantly. On the other hand, reaction with ketene silyl acetals **13c** and **13d**, gave the corresponding β-isomers **β-15c** and **β-15d** in about 90% selectivity.

Consequently, useful synthetic intermediates such as **15c** and **15d** for the synthesis of various *C*-nucleosides[12] were prepared in a highly β-selective manner by using the neighboring group participation of methylsulfinylethyl group on the 3-hydroxyl group. The 2-(methylsulfinyl)ethyl group was found to be easily removed after conversion to 2-(methylsulfonyl)-ethyl group by treatment with potassium *t*-butoxide in 1,2-dimethoxyethane at 0 °C.

Next, we applied this stereocontrol to prepare *S*-glycosides from 2-deoxyribofuranose. In the synthesis of *S*-glycosides, 2-(methylsulfinyl)ethyl group is not considered to be suitable because thioglycoside bond would be cleaved in the deprotecting process of the 2-(methylsulfinyl)ethyl group (oxidation followed by base treatment). 2-Pyridylmethyl group *N*-oxide was therefore chosen as a 3-*O*-protective group, and the reaction of **6e** with trimethlysilyl sulfides was tried in the presence of TMSOTf at −78 °C in dichloromethane, and the corresponding β-*S*-glycosides **β-17** were prepared predominantly as shown in the following table.



6e 17

Table 4. Reaction of **6e** with Trimethylsilyl Sulfides

17	R	Yield/%	α : β
17a	Et	83	16 : 84
17b	$PhCH_2$	77	25 : 75
17c	*i*-Pr	75	21 : 79
17d	t-Bu- 	82	35 : 65

In these reactions, better selectivity was also observed by employing silyl sulfide having better nucleophilicity such as ethyl trimethylsilyl sulfide. The produced β-ethylthioglycoside **β-17a** isomerized by treatment with $SnCl_4$ at 0 °C, and quenching the reaction after cooling to −78 °C afforded an α-major mixture (α:β=75:25). Consequently, the β-selectivity of the above *S*-glycosylation reaction at −78 °C is indicated to be controlled kinetically.

Furthermore, when 3-*O*-benzyl derivative **6a** was

Table 3. ^1H NMR Data of C-2 Protons of the *C*-Glycosides **15**

Compound	NMR data	
15a-α	1.81 (ddd, *J*=4.2, 5.8, 13.4 Hz),	2.52 (td, *J*=6.7, 13.4 Hz)
15a-β	1.72 (ddd, *J*=6.1, 10.4, 13.5 Hz),	2.30 (ddd, *J*=1.1, 5.2, 13.5 Hz)
15b-α	1.69 (ddd, *J*=4.2, 6.3, 13.3 Hz),	2.41 (td, *J*=6.6, 13.3 Hz)
15b-β	1.62 (ddd, *J*=6.1, 10.4, 13.3 Hz),	a)
15c-α	1.78 (b)),	2.35 (td, *J*=6.8, 13.4 Hz)
15c-β	1.72 (ddd, *J*=6.4, 10.1, 13.4 Hz),	2.13 (dd, *J*=5.2, 13.4 Hz)
15c'-α	1.83 (ddd, *J*=3.7, 5.5, 13.4 Hz),	2.39 (td, *J*=6.8, 13.4 Hz)
15c'-β	1.71 (ddd, *J*=6.2, 10.3, 13.4 Hz),	2.19 (dd, *J*=5.6, 13.4 Hz)
15d'-α	1.82 (b)),	2.40 (td, *J*=6.4, 13.3 Hz)
15d'-β	1.72 (ddd, *J*=6.7, 11.0, 13.4 Hz),	2.16 (ddd, *J*=1.2, 5.1, 13.4 Hz)
15e-α	a)	2.35 (td, *J*=7.7, 13.7 Hz)
15e-β	a)	2.02 (ddd, *J*=1.4, 4.9, 13.7 Hz)
15f-α	1.80 (ddd, *J*=4.7, 7.1, 13.3 Hz),	2.43 (td, *J*=6.2, 13.3 Hz)
15f-β	a)	2.02 (ddd, *J*=1.2, 5.0, 13.3 Hz)

a) Overlapped with other signals(s). b) Poorly resolved.

employed in the reaction with ethyl trimethylsilyl sulfide under the same reaction conditions, the product was isolated as a 1:1 mixture of the α- and β-isomers, These results apparently show that the neighboring group participation from 3-*O*-functionality plays the efficient role to control the stereochemistry in acid catalyzed glycosylation reactions.

Experimental

General. The IR spectra were determined on a Hitachi Model 260-30 spectrometer. The ^{1}H NMR spectra were recorded with Hitachi R-24B, JEOL GX-270, and/or JEOL GX-400 spectrometers in $CDCl_3$ with tetramethylsilane as an internal standard, unless otherwise noted. The optical rotations were carried out on a JMN DIP-181 polarimeter. HPLC analyses were performed on μPorasil P/N 27477 S/N or Resolve 5μ-silica with Shimadzu LC-6A system. All reactions except for hydrolysis were carried out under an anhydrous argon atmosphere. The reaction mixtures and combined extracts were dried over Na_2SO_4, if necessary, and concentrated in vacuo by an evaporator at 30—40 °C. Purification of products was performed by column chromatography on silica gel (Wakogel C-200 or Merck, Art. 9385 Kieselgel 60, 230—400 mesh). Acetonitrile, dichloromethane, HMPA, and *N,N*-dimethylformamide (DMF) were distilled from CaH_2 and stored over Molecular Sieves. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. Methanol was distilled with $Mg(OMe)_2$ and stored over Molecular Sieves. The 3-*O*-substituted 1-*O*-acetyl-5-*O*-benzyl-2-deoxy-D-ribofuranoses were prepared as their anomeric mixtures throughout the synthetic course, and the elemental analyses were carried out when samples were purified as each single isomer.

Methyl 5-*O*-*t*-Butyldimethylsilyl-2-deoxy-D-*erythro*-pentofuranoside (7). To a solution of methyl 2-deoxy-D-*erythro*-pentofuranoside[13] (**1**) (7.41 g, 50 mmol), triethylamine (6.37 g, 63 mmol), and 4-(dimethylamino)pyridine (DMAP) (cat. amount) in dichloromethane–DMF (10/1, v/v) (110 ml) was added *t*-butyldimethylsilyl chloride (7.91 g, 52 mmol) at 0 °C. After stirring at ambient temperature overnight, the mixture was quenched with pH 7 phosphate buffer and the organic layer was extracted with dichloromethane. The extract was washed with water and aqueous NaCl and dried. The dichloromethane solution was evaporated and the residue was purified by column chromatography (ethyl acetate:hexane=1:3, v/v) to give methyl 5-*O*-*t*-butyldimethylsilyl-2-deoxy-D-ribofuranoside (**7**) (10.81 g, 82%): α-isomer; $[\alpha]_D^{25}$ −87.1° (*c* 0.982, $CHCl_3$); IR(neat) 3400, 2920, 1100, 835, 780 cm^{-1}; ^{1}H NMR δ=0.05 (6H, s), 0.89 (9H, s), 1.73—2.43 (2H, m), 2.93 (1H, d, *J*=10.5 Hz), 3.40 (3H, s), 3.47—3.93 (2H, m), 3.93—4.43 (2H, m), 5.07 (1H, dd, *J*=1.5, 4.0 Hz); Found: C, 54.76; H, 10.13%. Calcd for $C_{12}H_{26}O_4Si$: C, 54.92; H, 9.99%. β-Isomer; $[\alpha]_D^{24.7}$ +85.8 (*c* 1.053, $CHCl_3$); IR(neat) 3400, 2920, 1100, 835, 780 cm^{-1}; ^{1}H NMR δ=0.08 (6H, s), 0.91 (9H, s), 1.83—2.37 (2H, m), 2.50 (1H, brs), 3.35 (3H, s), 3.47—4.37 (3H, m), 4.43 (1H, m), 5.07 (1H, dd, *J*=3.5, 5.5 Hz); Found: C, 54.66; H, 10.07%. Calcd for $C_{12}H_{26}O_4Si$: C, 54.92; H, 9.99%.

Alkylation of Hydroxy Compounds via Lithium Alkoxides: Methyl 5-*O*-*t*-Butyldimethylsilyl-2-deoxy-3-*O*-(diethylcarbamoyl)methyl-D-*erythro*-pentofuranoside (8). To a solution of monosilylated methyl furanoside (**7**) (17.92 g, 68.3 mmol) and NaI (10.2 g, 68 mmol) in THF (200 ml) was added slowly the solution of *n*-BuLi in hexane (45 ml, 68.2 mmol) at −78 °C, and the mixture was stirred at the same temperature for 30 min. After addition of HMPA (23.8 ml, 136 mmol) and freshly distilled *N,N*-diethy-1-bromoacetamide (11.6 ml, 81.9 mmol), the mixture was stirred at room temperature overnight. After addition of diethylamine (5 ml) and stirring for 1 h, pH 7 phosphate buffer was added, and the mixture was extracted with ether. The ether extract was washed with water and aqueous NaCl and dried. The ether solution was concentrated and the residue was purified by column chromatography (ethyl acetate:hexane=1:3—2:1, v/v) to give the alkylated silyl compound **8** (23.22 g, 91%): α-isomer; $[\alpha]_D^{26}$ +73.6° (*c* 1.09, $CHCl_3$); IR(neat) 2930, 1650, 1460, 1260, 1100, 840, 780 cm^{-1}; ^{1}H NMR δ=0.05 (6H, s), 0.88 (9H, s), 1.13 (6H, brt, *J*=7.0 Hz), 2.00—2.20 (2H, m), 3.32 (4H, q, *J*=7.0 Hz), 3.33 (3H, s), 3.53—3.75 (2H, m), 3.90—4.23 (2H, m), 4.10 (2H, s), 4.97 (1H, dd, *J*=2.8, 4.0 Hz); Found: C, 57.31; H, 10.01; N, 3.73%. Calcd for $C_{18}H_{37}NO_5Si$: C, 57.56; H, 9.93; N, 3.73%. β-Isomer; $[\alpha]_D^{22.6}$ −58.6° (*c* 0.517, $CHCl_3$); IR(neat) 2930, 1650, 1460, 1260, 1110, 840, 780 cm^{-1}; ^{1}H NMR δ=0.09 (6H, s), 0.90 (9H, s), 1.16 (6H, brt, *J*=7.0 Hz), 2.05—2.33 (2H, m), 3.05—3.80 (6H, m), 3.26 (3H, s), 3.80—4.28 (2H, m), 4.09 (2H, s), 5.03 (1H, t, *J*=4.2 Hz); Found: C, 57.32; H, 9.78; N, 3.76%. Calcd for $C_{18}H_{37}NO_5Si$: C, 57.56; H, 9.93; N, 3.73%.

Methyl 2-Deoxy-3-*O*-(diethylcarbamoyl)methyl-D-*erythro*-pentofuranoside (9). An 1 M-solution (1 M=1 mol dm^{-3}) of tetrabutylammonium fluoride in THF (6 ml, 6 mmol) was added to a solution of the above silyl compound **8** (1.88 g, 5.0 mmol) in THF (5 ml) at 0 °C and the mixture was stirred for 5 h at room temperature. Then the mixture was concentrated and purified by column chromatography (ethyl acetate:methanol=30:1—20:1, v/v) to give the hydroxy compound **9** (1.26 g, 96%): α-isomer; $[\alpha]_D^{26}$ +161.9° (*c* 1.461, $CHCl_3$); IR(neat) 3400, 2920, 1630, 1100 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.95—1.40 (6H, m), 1.80—2.40 (2H, m), 3.10—4.15 (9H, m), 3.30 (3H, s), 4.07 (2H, s) 4.90 (1H, dd, *J*=2.0, 5.2 Hz). β-Isomer; $[\alpha]_D^{26}$ −33.9° (*c* 0.577, $CHCl_3$); IR(neat) 3400, 2920, 1630, 1100 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.17 (6H, brt, *J*=7.0 Hz), 1.90—2.23 (2H, m), 2.70 (1H, br), 3.10—3.80 (6H, m), 3.25 (3H, s), 3.80—4.30 (2H, m), 4.07 (2H, s), 4.93 (1H, dd, *J*=2.5, 4.7 Hz).

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-(diethylcarbamoyl)methyl-D-*erythro*-pentofuranoside (*10*). Alkylation of methyl 2-deoxy-3-*O*-(diethylcarbamoyl)methyl-D-*erythro*-pentofuranoside (**9**) (1.20 g, 4.6 mmol) with benzyl bromide (0.94 g, 5.5 mmol) in the same manner as mentioned before gave the benzylated compound **10** (1.40 g, 87%): α-isomer; $[\alpha]_D^{24.5}$ + 90.6° (*c* 0.980, $CHCl_3$); IR(neat) 2940, 1650, 1370, 1210, 1110, 740, 700 cm^{-1}; ^{1}H NMR δ=1.10 (6H, t, *J*=7.0 Hz), 1.80—2.70 (2H, m), 3.05—3.70 (4H, m), 3.37 (3H, s), 3.60 (2H, d, *J*=6.0 Hz), 3.87—4.43 (2H, m), 4.10 (2H, s), 4.54 (2H, s), 5.03 (1H, dd, *J*=2.2, 4.7 Hz), 7.26 (5H, s); Found: C, 64.65; H, 8.50; N, 3.90%. Calcd for $C_{19}H_{29}NO_5$: C, 64.94; H, 8.32; N, 3.99% β-Isomer; $[\alpha]_D^{26}$ −57.0° (*c* 0.965, $CHCl_3$); IR(neat) 2940, 1650, 1370, 1210, 1110, 740, 700 cm^{-1}; ^{1}H NMR δ=1.10 (6H, t, *J*=7.0 Hz), 2.00—2.35 (2H, m), 2.90—3.60 (6H, m), 3.28 (3H, s), 4.07 (2H, s), 3.96—4.40 (2H, m), 4.52 (2H, s), 5.02 (1H, t, *J*=3.8 Hz), 7.26 (5H, s); Found: C, 64.78; H, 8.55; N, 3.76%. Calcd for $C_{19}H_{29}NO_5$: C, 64.94; H, 8.32; N, 3.99%.

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-hydroxy)ethyl-D-*ery*-

thro-**pentofuranoside (11).** A slurry of the amide **10** (6.06 g 17.2 mmol), *t*-BuOK (12.76 g, 114 mmol), and water (0.62 ml, 34 mmol) in THF (170 ml) was stirred vigorously at room temperature overnight.[14] After addition of ice and water, the mixture was washed with ether. Aqueous layer was acidified with aqueous 2 M $KHSO_4$ and extracted with ether for five times. The ether extract was dried over $MgSO_4$ and evaporated to give the crude carboxylic acid.

To a suspension of lithium aluminum hydride (653 mg, 17.2 mmol) in THF (52 ml) was added dropwise a solution of the above carboxylic acid in THF (10 ml) at 0 °C, and the mixture was stirred at room temperature overnight. To this mixture was added carefully ethyl acetate followed by aqueous 30%-Rochelle salt, and the mixture was extracted with ether. The ether extract was dried and evaporated. Purification of the residue by column chromatography (ethyl acetate:hexane=2:1—1:0, v/v) gave the 2-hydroxyethyl compund **11** (4.15 g, 85%): α-isomer; $[\alpha]_D^{22.5}$ +94.6° (*c* 2.16, $CHCl_3$); IR(neat) 3450, 2900, 1450, 1360, 1200, 1100, 730, 690 cm^{-1}; ^1H NMR δ=1.90—2.25 (2H, m), 2.53 (1H, br), 3.20—4.40 (8H, m), 3.36 (3H, s), 4.52 (2H, s), 5.03 (1H, m), 7.25 (5H, s). β-Isomer; $[\alpha]_D^{22}$ −49.8° (*c* 0.765, $CHCl_3$); IR(neat) 3450, 2900, 1450, 1360, 1200, 1100, 730, 690 cm^{-1}; ^1H NMR δ=2.00—2.30 (2H, m), 2.55 (1H, br), 3.26 (3H, s), 3.30—3.80 (6H, m), 3.80—4.30 (2H, m), 4.52 (2H, s), 5.02 (1H, dd, *J*=2.6, 4.6 Hz), 7.27 (5H, s).

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylthio)ethyl]-D-*erythro*-pentofuranoside (12f). To a solution of the hydroxyethyl compound **11** (2.30 g, 8.2 mmol) and triethylamine (1.5 g, 14.7 mmol) in dichloromethane (30 ml) was added slowly methanesulfonyl chloride (1.4 g, 12.2 mmol) at 0 °C, and stirred at the same temperature for 30 min. After addition of pH 7 phosphate buffer, the mixture was extracted with ether. The ether extract was dried and evaporated to give the corresponding mesylate.

To a solution of dimethyl disulfide (1.62 ml, 18 mmol) in ethanol (10 ml) was added sodium borohydride (680 mg, 18 mmol) at 0 °C, and the above mesylate was added to the mixture and the resulting mixture was stirred at room temperature overnight. After evaporation of the solvent, followed by addition of water, the mixture was extracted with dichloromethane. The extract was dried and evaporated. The residue was purified by column chromatography (ethyl acetate:hexane=1:3, v/v) to afford 2-(methylthio)ethyl compound **12f** (1.71 g, 91%): α-isomer; $[\alpha]_D^{29}$ +106.7° (*c* 0.588, $CHCl_3$); IR(neat) 2900, 1445, 1360, 1200, 1100, 730, 690 cm^{-1}; ^1H NMR δ=1.95 (3H, s), 1.60—2.10 (2H, m), 2.48 (2H, t, *J*=7.0 Hz), 3.23 (3H, s), 3.30—4.16 (6H, m), 4.45 (2H, s), 4.91 (1H, dd, *J*=2.0, 5.6 Hz), 7.27 (5H, s); Found: C, 61.41; H, 7.84%. Calcd for $C_{16}H_{24}O_4S$: C, 61.51; H, 7.74%. β-Isomer; $[\alpha]_D^{29}$ −43.9° (*c* 1.154, $CHCl_3$); IR(neat) 2900, 1445, 1360, 1200, 1100, 730, 690 cm^{-1}; ^1H NMR δ=2.07 (3H, s), 1.70—2.30 (2H, m), 2.60 (2H, t, *J*=7.0 Hz), 3.26 (3H, s), 3.35—3.73 (4H, m), 3.80—4.30 (2H, m), 4.52 (2H, s), 5.00 (1H, dd, *J*=2.4, 4.4 Hz), 7.25 (5H, s); Found: C, 61.51; H, 7.78%. Calcd for $C_{16}H_{24}O_4S$: C, 61.51; H, 7.74%.

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfinyl)ethyl]-D-*erythro*-pentofuranoside. To a solution of the methylthio compound **12f** (367 mg, 1.17 mmol) in methanol was added a solution of sodium periodate (265 mg, 1.23 mmol) in water (0.5 ml), and stirred at room temperature overnight. After separation of inorganic precipitates, the filtrate was diluted with dichloromethane and dried. Evaporation of the solution and purification by column chromatography (ethyl acetate:hexane:methanol=5:3:1, v/v/v) gave the methylsulfinyl compound (384 mg, 100%): α-isomer; IR(neat) 2900, 1450, 1360, 1100, 1050, 740, 700 cm^{-1}; ^1H NMR δ=2.00—2.50 (2H, m), 2.55 (3H, s), 2.80—3.10 (2H, m), 3.40 (3H, s), 3.50—3.70 (2H, m), 3.86 (2H, t, *J*=7.4 Hz), 3.95—4.40 (2H, m), 4.60 (2H, s), 5.05 (1H, dd, *J*=2.0, 5.0 Hz), 7.30 (5H, s). β-Isomer; IR(neat) 2900, 1450, 1360, 1100, 1050, 740, 700 cm^{-1}; ^1H NMR δ=1.90—2.40 (2H, m), 2.55 (3H, s), 2.70—3.10 (2H, m), 3.36 (3H, s), 3.40—3.70 (2H, m), 3.80 (2H, t, *J*=7.6 Hz), 3.97—4.35 (2H, m), 4.53 (2H, s), 5.01 (1H, dd, *J*=3.0, 4.6 Hz), 7.26 (5H, s).

1-*O*-Acetyl5-*O*-benzyl-2-deoxy-3-*O*-[(2-methylsulfinyl)-ethyl]-D-*erythro*-pentofuranose (6h). A vigorously stirred mixture of methyl 5-*O*-benzyl-2-deoxy-3-*O*-[(2-methylsulfinyl)ethyl]-D-*erythro*-pentofuranoside (**12f**) (1.47 g, 4.5 mmol) and Dowex 50-X8 (10 ml) in THF-water (2/1, v/v, 12 ml) was maintained at 45 °C for 5 h. After separation of the resin, the filtrate was extracted with dichloromethane. The extract was dried and evaporated to give a residue. To a solution of this residue, pyridine (0.36 ml, 4.5 mmol), and DMAP (67 mg 0.5 mmol) in dichloromethane (10 ml) was added acetic anhydride (0.64 ml, 6.8 mmol) at 0 °C. After stirring the mixture for 1 h at room temperature, the mixture was evaporated and purified by column chromatography (ethyl acetate:hexane:methanol=5:3:1, v/v/v) to give the desired acetate **6h** (1.30 g, 81%): IR(neat) 2900, 1735, 1370, 1240, 1100, 1050, 740, 700 cm^{-1}; ^1H NMR δ=1.93 (2/3×3H, s), 2.02 (1/3×3H, s), 2.10—2.45 (2H. m), 2.55 (2/3×3H, s), 2.58 (1/3×3H, s), 2.70—3.00 (2H, m), 3.51 (2H, d, *J*=5.0 Hz), 3.82 (2H, t, *J*=5.5 Hz), 3.93—4.37 (2H, m), 4.47 (1/3×2H, s), 4.52 (2/3×2H, m), 6.23 (1H, m), 7.26 (5H, s).

Methyl 3,5-Bis[*O*-(*t*-butyldimethylsilyl)]-2-deoxy-D-*erythro*-pentofuranoside (2). This compound was prepared from 2-deoxy-D-ribose by the same procedure used for the compound **7** except for using 2.6 equiv of *t*-butyldimethylsilyl chloride and 3.0 equiv of triethylamine in 87% yield. IR(neat) 2950, 1480, 1260, 1120, 840, 780 cm^{-1}; ^1H NMR δ=0.08 (12H, s), 0.88 (18H, s), 1.53—2.65 (2H, m), 3.33 (1/3×3H, s), 3.36 (2/3×3H, s), 3.50—4.10 (3H, m), 4.10—4.62 (1H, m), 4.85—5.18 (1H, m).

Methyl 3-*O*-*t*-Butyldimethylsilyl-2-deoxy-D-*erythro*-pentofuranoside (3). A solution of the disilyl compound **2** (25.6 g, 68 mmol) and pyridinium *p*-toluenesulfonate (1.58 g, 6.3 mmol) in methanol (80 ml) was stirred at room temperature for 1 d. After addition of aqueous Na_2CO_3, the reaction mixture was concentrated followed by extraction with dichloromethane. The extract was washed with water and then aqueous NaCl, dried, and evaporated. Separation of the residue by column chromatography (ethyl acetate:hexane=1:5—1:1, v/v) gave the recovered starting disilyl compound **2** (8.5 g, 33% recovered) and the desired 3-*O*-monosilylated compound **3** (9.75 g, 55%): α-isomer; IR(neat) 3400, 2930, 1460, 1250, 1100, 840, 790 cm^{-1}; ^1H NMR δ=0.05 (6H, s), 0.89 (9H, s), 1.73(1H, ddd, *J*=3.0, 6.0, 13.5 Hz), 2.27 (1H, ddd, *J*=5.5, 8.0, 13.5 Hz), 2.37 (1H, s), 3.27 (3H, s), 3.33—3.87 (3H, m), 4.13 (1H, dt, J_d=8.0 Hz, J_t=6.0 Hz), 4.83 (1H, dd, *J*=3.0, 5.5 Hz). β-Isomer; IR(neat) 3400, 2930, 1250, 1100, 840 cm^{-1}; ^1H NMR δ=0.07 (6H, s), 0.87 (9H, s), 1.67—2.23 (2H, m), 2.30 (1H, t, *J*=6.0 Hz), 3.28 (3H, s), 3.33—3.67 (2H, m), 3.80 (1H, m), 4.38 (1H, dt, J_d=4.0 Hz, J_t=6.0 Hz), 4.92 (1H, dd, *J*=2.5, 4.5 Hz).

Methyl 5-*O*-Benzyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-D-*ery*-

thro-pentofuranoside (**4**). According to the method for alkylation, the 3-*O*-monosilylated compound **3** was alkylated by benzyl bromide to the 5-*O*-benzyl-3-*O*-silyl derivative **4** in 92% yield: IR(neat) 2900, 1470, 1360, 1260, 1100, 840, 780, 700 cm^{-1}; ^1H NMR δ=0.05 (6H, s), 0.83 (9H, s), 1.50—2.62 (2H, m), 3.27 (1/2×3H, s), 3.33 (1/2×3H, s), 3.40—3.66 (2H, m), 3.70—4.45 (2H, m), 4.51 (2H, s), 4.80—5.10 (1H, m), 7.22 (5H, s).

Methyl 5-*O*-Benzyl-2-deoxy-D-*erythro*-pentofuranoside (5). Compound **5** was prepared from the above 5-*O*-benzyl-3-*O*-silyl compound **4** by the same procedure used for the compound **9** in 98% yield: IR(neat) 3450, 2900, 1100, 740, 700 cm^{-1}; ^1H NMR δ=1.80—2.14 (2H, m), 2.45—3.00 (1H, m), 3.27 (2/5×3H, s), 3.35 (3/5×3H, s), 3.30—3.60 (2H, m), 3.60—4.30 (2H, m), 4.44 (2H, brs), 4.75—4.98 (1H, m), 7.26 (5H, s).

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-D-*erythro*-pentofuranoside *N*-Oxide. To a mixture of the methyl 5-*O*-benzyl-2-deoxyriboside **5** (480 mg, 2 mmol), sodium iodide (750 mg, 5 mmol), and *t*-butyl alcohol (296 mg, 4 mmol) in THF (7 ml) was added 60% sodium hydride (240 mg, 6 mmol), and the mixture was stirred for 1 h at room temperature. Then 2-(chloromethyl)pyridine *N*-oxide hydrochloride (558 mg, 3 mmol) was added to the mixture are the resulting mixture was stirred for 12 h at room temperature. After addition of pH 7 phosphate buffer, the organic compounds were extracted with the combined solvent (ether:ethanol=20:1, v/v). The extract was dried and evaporated. Purification of the residue by column chromatography (ethyl acetate:hexane:methanol=5:3:1, v/v/v) gave the titled compound (624 mg, 90%): IR(neat) 2920, 1500, 1435, 1360, 1250, 1100, 1050, 860, 770, 740, 700 cm^{-1}; ^1H NMR δ=2.00—2.33 (2H, m), 3.25 (2/5×3H, s), 3.33 (3/5×3H, s), 3.40—3.70 (2H, m), 3.90—4.45 (2H, m), 4.50 (2H, s), 4.69 (2H, s), 4.90—5.15 (1H, m), 6.95—7.70 (8H, m), 7.90—8.22 (1H, m).

1-*O*-Acetyl-5-*O*-benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-D-*erythro*-pentofuranose *N*-Oxide (6e). According to the procedure used for the compound **6h**, methyl 5-*O*-benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-D-*erythro*-pentofuranoside *N*-oxide was hydrolyzed then acetylated to give the 1-*O*-acetyl compound **6e** in 85% yield: IR(neat) 2900, 1730, 1480, 1420, 1360, 1230, 1100, 1000, 840, 760, 730, 690 cm^{-1}; ^1H NMR δ=1.93 (2/3×3H, s), 2.00 (1/3×3H, s), 2.10—2.50 (2H, m), 3.40—3.70 (2H, m), 4.10—4.60 (2H, m), 4.53 (2H, s), 4.73 (2H, s), 6.22—6.40 (1H, m), 6.90—7.60 (8H, m), 8.05—8.30 (1H, m).

Other 3-*O*-substituted 5-*O*-benzyl-2-deoxy-D-*erythro*-pentofuranosides listed in Table 1 were prepared by the essentially same procedure described above.

***C*-Glycosylation Reaction: Benzyl 5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosylacetate (15c).** To a solution of methylsulfinyl compound (**6h**) (188 mg, 0.53 mmol) and 1-benzyloxy-1-(*t*-butyldimethylsilyloxy)ethylene (**13c**) (177 mg, 0.67 mmol) in dichloromethane (10 ml) was added a solution of TMSOTf (178 mg, 0.80 mmol) in dichloromethane (2 ml) slowly at −78 °C, and the mixture was stirred for 12 h at this temperature. The reaction mixture was quenched by addition of pH 7 phosphate buffer and the mixture was extracted with dichloromethane. The dichloromethane extract was dried and evaporated. After purification of the residue by column chromatography (ethyl acetate:hexane:methanol=5:3:1, v/v/v), the products were dissolved in methanol (10 ml) and oxidized by 10% H_2O_2 (10 ml) at room temperature in the presence of ammonium molybdate (VI) tetrahydrate (100 mg, 0.08 mmol) at room temperature. The reaction mixture was extracted with dichloromethane and dried, then followed by evaporation of the solvent. Purification of the residue by column chromatography (ethyl acetate:hexane=2:1, v/v) gave the mixture of the isomers of the *C*-glycoside **15c** (220 mg, 86%) (α:β=9:91): IR(neat) 2900, 1730, 1450, 1300, 1100, 740, 690 cm^{-1}; ^1H NMR δ=1.72 (9/10×1H, ddd, J=6.4, 10. 1, 13.4 Hz), 1.78 (1/10×1H, m), 2.13 (9/10×1H, dd, J=5.2, 13.4 Hz), 2.39 (1/10×1H, td, J_t=6.8 Hz, J_d=13.4 Hz), 2.57 (1H, dd, J=6.5, 15.8 Hz), 2.72 (1H, dd, J=6.5, 15.8 Hz), 2.88 (1/10×3H, s), 2.92 (9/10×3H, s), 3.17 (2H, t, J=5.6 Hz), 3.38 (1H, dd, J=6.2, 10.2 Hz), 3.53 (1H, dd, J=4.3, 10.2 Hz), 3.82 (1H, dd, J=6.5, 11.7 Hz), 3.86 (1H, dd, J=5.6, 11.7 Hz), 3.96—4.01 (1H, m), 4.01—4.07 (1H, m), 4.37—4.48 (1H, m), 4.52 (2H, s), 5.13 (2H, s), 7.25—7.38 (10H, m).

The characteristic patterns of C-2 protons in NMR spectrum were summerized in Table 3 together with those of the other *C*-glycosides.

2-[5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]-1-phenylethanone (15a): IR(neat) 2920, 1680, 1600, 1450, 1310, 1130, 740, 695 cm^{-1}; ^1H NMR δ=1.50—2.50 (2H, m), 2.89 (1/3×3H, s), 2.96 (2/3× 3H, s), 3.00—3.26 (4H, m), 3.40—3.58 (2H, m), 3.77—4.44 (4H, m), 4.53 (2H, s), 4.55—4.85 (1H, m), 7.25—7.65 (8H, m), 7.90—8.10 (2H, m).

1-[5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]-2-propanone (15b): IR(neat) 2900, 1710, 1310, 1290, 1130, 1100, 740, 700 cm^{-1}; ^1H NMR δ=1.40—2.40 (2H, m), 2.16 (3H, s), 2.50—2.90 (1H, m), 2.92 (3H, s), 3.00—3.60 (4H, m), 3.70—4.10 (4H, m), 4.10—4.50 (1H, m), 4.51 (2H, s), 7.30 (5H, s).

Methyl 2-[5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]glycolate (15d): IR(neat) 3470, 2900, 1735, 1120, 740, 700 cm^{-1}; ^1H NMR δ=1.60—2.45 (2H, m), 2.90 (3H, s), 3.00—3.65 (5H, m), 3.70—4.60 (9H, m), 4.50 (2H, s), 7.26 (5H, s).

Methyl 5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosylacetate (15d′). To a solution of methyl 2-[5-*O*-benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]glycolate (**15d**) (78 mg, 0.19 mmol), triethylamine (50 mg, 0.35 mmol), and DMAP (cat. amount) in anhydrous acetonitrile (3 ml) was added phenyl carbonochloridothioate (60 mg, 0.35 mmol) at 0°C and the solution was stirred at room temperature for 1 d. After addition of pH 7 phosphate buffer, the mixture was extracted with dichloromethane. The extract was dried and evaporated. The residue was purified by column chromatography (ethyl acetate:hexane=2:1, v/v) to give corresponding thiocarbonate (74 mg, 77%): ^1H NMR δ=1.75—2.40 (2H, m), 2.90 (3H, s), 3.00—3.60 (4H, m), 3.65—4.30 (6H, m), 4.48 (2H, s), 4.30—4.80 (1H, m), 5.56 (1H, dd, J=3.6 Hz, 8.0 Hz), 6.90—7.60 (5H, m), 7.25 (5H, s).

A solution of the thiocarbonate obtained above (74 mg, 0.146 mmol), tributyltin hydride (47 mg., 0.162 mmol), and azobisisobutyronitrile (cat. amount) in dry toluene (5 ml) was heated under reflux for 2 h. Evaporation of the mixture and purification of the residue by column chromatography (ethyl acetate:hexane=1:2, v/v) gave the deoxygenated compound (**15d′**) (42 mg, 75%): IR(neat) 2900, 1735, 1100, 745, 705 cm^{-1}; ^1H NMR δ=1.72 (9/10×1H, ddd, J=6.7, 11.0,

13.4 Hz), 1.82 (1/10×1H, m), 2.16 (9/10×1H, ddd, J=1.2, 5.1, 13.4 Hz), 2.40 (1/10×1H, td, J_t=6.4 Hz, J_d=13.3 Hz), 2.53 (1H, dd, J=6.1, 15.6 Hz), 2.67 (1H, dd, J=6.9, 15.6 Hz), 2.94 (1/10×3H, s), 2.96 (9/10×3H, s), 3.19 (2H, t, J=5.5 Hz), 3.41 (1H, dd, J=5.8, 10.0 Hz), 3.55 (1H, dd, J=4.6, 10.0 Hz), 3.68 (3H, s), 3.78—3.93 (2H, m), 3.97—4.18 (2H, m), 4.53 (2H, s), 7.27—7.42 (5H, m).

Methyl 2-[5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]-2,2-dimethoxyacetate (15e): IR(neat) 2900, 1740, 1300, 1100, 735, 700 cm^{-1}; ^{1}H NMR δ=1.60—2.40 (2H, m), 2.85 (3H, s), 3.23 (2/5×6H, s), 3.33 (3/5×6H, s), 3.61 (3/5×3H, s), 3.71 (2/5×3H, s), 2.90—4.30 (9H, m), 4.43 (2H, s), 7.20 (5H, s).

3-[5-*O*-Benzyl-2-deoxy-3-*O*-[(2-methylsulfonyl)ethyl]-D-*erythro*-pentofuranosyl]-1-propene (15f): IR(neat) 2900, 1640, 1310, 1290, 1100, 740, 700 cm^{-1}; ^{1}H NMR δ=1.58—1.76 (1H, m), 1.96—2.50 (3H, m), 2.93 (3H, s), 3.18 (2H, t, J=5.4 Hz), 3.36—3.58 (2H, m), 3.77—3.92 (2H, m), 3.97—4.18 (3H, m), 4.55 (2H, s), 5.03—5.15 (2H, m), 5.72—5.88 (1H, m), 7.25—7.38 (5H, m).

(1*R*,6*R*,8*S*)-8-[(2-Methylsulfonyl)ethyl]-3,9-dioxabicyclo-[4.2.1]nonan-4-one (16). The dibenzyl *C*-glycoside **15c** (100 mg, 0.22 mmol) was hydrogenated with 10%-Pd/C (20 mg) in ethanol (1 ml) at 50 °C for 12 h. Separation of the catalyst and evaporation gave the corresponding hydroxy carboxylic acid **15c′** in quantitative yield: IR(neat) 3400, 2950, 1720, 1400, 1280, 1130, 1100, 960, 820, 740 cm^{-1}; ^{1}H NMR (CD_3OD) δ=1.71 (9/10×1H, ddd, J=6.2 10.3, 13.4 Hz), 1.83 (1/10×1H, m), 2.19 (9/10×1H, dd, J=5.6, 13.4 Hz), 2.39 (1/10×1H, m), 2.56 (2H, d, J=6.4 Hz), 3.02 (3H, s), 3.35 (2H, t, J=5.4 Hz), 3.51 (1H, dd, J=5.6, 11.5 Hz), 3.56 (1H, dd, J=5.1, 11.5 Hz), 3.82—3.94 (3H, m), 4.00—4.04 (1H, m), 4.42—4.57 (1H, m).

A solution of the above carboxylic acid **15c′** (33 mg, 0.12 mmol) and acetic anhydride (12 μl, 0.13 mmol) in anhydrous pyridine (12 ml) was heated under reflux for 12 h. The reaction mixture was condensed and purified by silica-gel preparative TLC (ethyl acetate) to give the lactone **16** (14 mg, 45%): IR (CH_2Cl_2) 1740, 1310, and 1100 cm^{-1}; ^{1}H NMR δ=2.15—2.30 (2H, m), 2.89 (1H, dd, J=5.1, 16.5 Hz), 2.98 (3H, s), 3.03 (1H, d, J=16.5 Hz), 3.19—3.24 (2H, m), 3.80—3.93 (2H, m), 4.28 (1H, dd, J=4.0, 13.6 Hz), 4.37 (1H, d, J=13.6 Hz), 4.40—4.45 (2H, m), 4.57—4.63 (1H, m).

S-Glycosilation reactions were performed with essentially the same procedure as the *C*-glycosylation reaction. The IR and NMR data of the *S*-glycosylation products listed in Table 3 are as follows:

Ethyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-1-thio-D-*erythro*-pentofuranoside *N*-Oxide (17a): IR(neat) 2850, 1500, 1440, 1360, 1230, 1100, 840, 760, 735, 690 cm^{-1}; ^{1}H NMR δ=1.30 (0.84×3H, t, J=7.5 Hz), 1.32 (0.16×3H, t, J=7.5 Hz), 2.07 (0.16×1H, m), 2.13 (0.84×1H, ddd, J=5.6, 8.6, 13.3 Hz), 2.43 (0.84×1H, ddd, J=3.4 6.0, 13.3 Hz), 2.60—2.80 (2.16H, m), 3.56 (1H, dd, J=6.0, 15.0 Hz), 3.66 (1H, dd, J=5.6, 15.0 Hz), 4.15—4.32 (2H, m), 4.57 (2H, s), 4.74 (1H, d, J=15.5 Hz), 4.82 (1H, d, J=15.5 Hz), 5.40 (0.84×1H, dd, J=6.0, 8.6 Hz), 5.53 (0.16×1H, dd, J=3.7, 7.6 Hz), 7.16—7.40 (7H, m), 7.49—7.63 (1H, m), 8.20 (1H, m).

Benzyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-1-thio-D-*erythro*-pentofuranoside *N*-Oxide (17b): IR(neat) 2870, 1485, 1425, 1240, 1085, 850, 760, 730, 690 cm^{-1}; ^{1}H NMR δ=2.02 (0.25×1H, td, J_t=3.0 Hz, J_d=14.2 Hz), 2.15 (0.75×1H, ddd, J=6.4, 7.8, 13.9 Hz), 2.37 (0.75×1H, ddd, J=2.9, 6.4, 13.9 Hz), 2.58 (0.25×1H, td, J_t=7.6 Hz, J_d=14.2 Hz), 3.59 (1H, dd, J=6.0, 13.5 Hz), 3.68 (1H, dd, J=5.0, 13.5 Hz), 3.82 (0.25×1H, d, J=13.5 Hz), 3.83 (0.75×1H, d, J=13.5 Hz), 3.93 (0.25×1H, d, J=13.5 Hz), 3.94 (0.75×1H, d, J=13.5 Hz), 4.13—4.47 (2H, m), 4.58 (2H, s), 4.75 (2H, s), 5.28 (0.75×1H, dd, J=6.4, 7.7 Hz), 5.37 (0.25×1H, dd, J=3.0, 7.6 Hz), 7.14—7.38 (12H, m), 7.45—7.63 (1H, m), 8.20 (1H, m).

Isopropyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-1-thio-D-*erythro*-pentofuranoside *N*-Oxide (17c): IR(neat) 2900, 1490, 1430, 1240, 1085, 850, 765, 740, 700 cm^{-1}; ^{1}H NMR δ=1.30 (6H, d, J=7.0 Hz), 1.95—2.18 (1H, m), 2.40—2.78 (1H, m), 3.18 (1H, m), 3.54 (1H, m), 3.66 (1H, m), 4.13—4.43 (2H, m), 4.58 (2H, s), 4.73 (1H, d, J=14.0 Hz), 4.82 (1H, d, J=14.0 Hz), 5.45 (0.79×1H, dd, J=6.2, 8.6 Hz), 5.58 (0.21×1H, dd, J=3.7, 8.1 Hz), 7.16—7.38 (7H, m), 7.48—7.55 (1H, m), 8.22 (1H, m).

4-*t*-Butylphenyl 5-*O*-Benzyl-2-deoxy-3-*O*-(2-pyridylmethyl)-1-thio-D-*erythro*-pentofuranoside *N*-Oxide (17d): IR(neat) 2950, 1420, 1240, 1100, 1080, 840, 760, 730, 690 cm^{-1}; ^{1}H NMR δ=1.29 (0.35×9H, s), 1.30 (0.65×9H, s), 2.10—2.32 (1H, m), 2.40—2.80 (1H, m), 3.56—3.68 (2H, m), 4.20—4.40 (2H, m), 4.48—4.65 (2H, m), 4.75—4.85 (2H, m), 5.58 (0.65×1H, dd, J=6.2, 9.0 Hz), 5.73 (0.35×1H, dd, J=3.1, 7.3 Hz), 7.15—7.35 (9H, m), 7.43—7.68 (3H, m), 8.18—8.33 (1H, m).

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