October, 1986] *Bull. Chem. Soc. Jpn.*, *59*, *3137—3143 (1986)* 3137

Synthetic Studies on Glycocinnamoylspermidine. II.[1] Synthesis of 4-*O*-(2-Azido-2-deoxy-D-xylopyranosyl)-2-azido-2-deoxy-D-xylopyranose Derivatives

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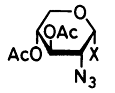
(Received April 8, 1986)

Synthetic intermediates for the aminopentose disaccharide moiety of glycocinnamoylspermidine were synthesized from D-xylose.

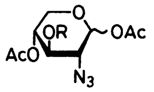
2-Amino-2-deoxy-D-xylose and 2,3-diamino-2,3-dideoxy-D-xylose, which are rare components in the field of carbohydrate antibiotics, constitute the disaccharide moiety of glycocinnamoylspermidine (cinodine)[2] in which the disaccharide is linked through a unique ureylene linkage with *p*-(bacillosaminyloxy)cinnamoylspermidine. In this paper we should like to report a detail of the previous comminucation[3] on the synthesis of the disaccharide. The synthesis of the *p*-(bacillosaminyloxy)cinnamate moiety was previously reported.[1]

First of all the synthesis of 2-azido-2-deoxy-D-xylopyranose disaccharide having β(1→4) glycosidic linkage was examined. In order to reduce the kinds of necessary protecting groups for amino function, the 2-azido group, albeit having no anchimeric assistance for the formation of the interglycosidic β-linkage, seems to be convenient. This substituent have also been considered as favorable for the formation of α-ureylene linkage at the reducing end, which was, however, recently revised to be β.[4] Moreover, the authors showed easy availability of 2-azido-2-deoxypentose derivatives in the preceding paper.[5] Three disaccharides (**14**, **15**, and **34**) were chosen as feasible starting compounds for the construction of the aminopentose disaccharide moiety.

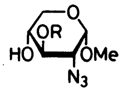
The Koenigs-Knorr method[6,7] and trimethylsilyl triflate (TMSOTf) method[8] were examined using 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranosyl halides (**1** and **2**) or 1,3,4-tri-*O*-acetyl-2-azido-2-deoxy-D-xylopyranose (**6**) as glycosyl donor, and methyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (**8**) or the corresponding 3-*O*-tetrahydropyranyl (THP) derivative (**9**) as glycosyl acceptor. The latter acceptor was prepared by treatment of methyl 2-azido-4-*O*-benzoyl-2-deoxy-α-D-xylopyranoside with 3,4-dihydropyran and pyridinium *p*-toluenesulfonate, followed by debenzoylation. In the Koenigs-Knorr reaction of glycosyl halide having no participating group at C-2, β-glycoside formation are favored generally by the use of insoluble silver salts such as silver carbonate and silver silicate, or mercury(II) salts such as mercuric cyanide and mercury(II) bromide, which have weak affinity for halogens to promote the S_N2 type substitution of α-halide. Both types of promoters, however, proved to be not effective for **1** and **2** as shown in Table 1. In the coupling of α-chloride (**1**) with **8** a mixture of α-linked (**12**) and β-linked disaccharide (**14**) was obtained only using mercury(II) cyanide in a polar solvent in a very low yield. Even in the



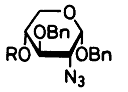
1 X=Cl
2 X=Br
3 X=OMe
4 X=OBn
5 X=OBz



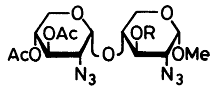
6 R=Ac
7 R=Bn



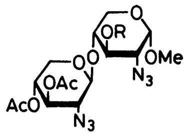
8 R=Bn
9 R=THP



10 R=H
11 R=Ac



12 R=Bn
13 R=THP



14 R=Bn
15 R=THP

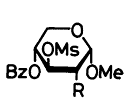
Table 1. Disaccharide Formation

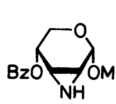
Donor	Acceptor	Reaction condition			Product and Yield/%	
		Promoter	Solvent	Temp/°C	α	β
1	**8**	$AgClO_4$, TMP	CH_3NO_2	−10	**12** 33	**14** 40
1	**8**	$Hg(CN)_2$	CH_3NO_2	60	**12** 5.3	**14** 4.7
1	**9**	$AgClO_4$, TMP	CH_3NO_2	−10	**13** 41	**15** 6
2	**9**	Ag_2CO_3	CH_2Cl_2	RT	**13** 16	
2	**9**	Ag_2O, I_2	CH_2Cl_2	RT	**13** 10	
2	**9**	HgO, $HgBr_2$	CH_2Cl_2	RT	**13** 11	
6	**8**	TMSOTf	$ClCH_2CH_2Cl$	0	**12** 16	**14** 36
1	**10**	$AgClO_4$, TMP	CH_3NO_2	RT	**33** 29	**35** 46

TMP: 2,4,6-Trimethylpyridine.

coupling of the more reactive α-bromide (**2**) with **9** only the α-linked disaccharide (**13**) was obtained in low yield with assistance of silver carbonate, silver oxide or mercury(II) bromide. Thus, 2-azido-2-deoxypentopyranosyl residue seems to be less reactive than the corresponding hexopyranosyl one. Therefore, glycosylation with silver perchlorate in nitromethane was examined in the presence of 2,4,6-trimethylpyridine. This method was proved to be suitable for β-glycoside formation in the cases of 3,4,6-triacetate of 2-*O*-benzyl- and 2-chloro-2-deoxy-α-D-glucopyranosyl chlorides.[9] The coupling of **1** and **8** gave **12** and **14** with predominance of the latter (4:5) in 73% yield, while the coupling of **1** with the benzyl glycoside (**10**) under the same conditions showed a slightly better selectivity to give a mixture of **32** and **34**, which were separated as *O*-deacetylated derivatives **33** and **35** in 29 and 46% yields, respectively. On the other hand, coupling of **1** with 3-*O*-THP derivative **9** exhibited a reverse selectivity to give α-linked (**13**) and β-linked disaccharide (**15**) in 41 and 6% yields, respectively. The result may be attributed to the lower reactivity of the 4-hydroxyl group in **9** due to the steric hindrance of bulky 3-*O*-THP moiety. Furthermore, coupling of 1-acetate (**6**) and **8** in the presence of TMSOTf gave **12** and **14** also with predominance of the latter (4:9) in 52% yield, respectively, to indicate a better selectivity for the formation of β-glycosidic linkage, albeit slightly in a lower yield. Considering that **6** consisted of almost α-anomer, S_N2 type substitution may predominate in this glycosylation.

Then, a precursor (**19**) of 2,3-diamino-2,3-dideoxy-D-xylose was derived via a 2,3-epimino derivative (**18**). 3-Mesylate (**16**) of methyl 2-azido-4-*O*-benzoyl-2-deoxy-α-D-xylopyranoside was hydrogenolyzed in the presence of platinum oxide to give 2-amino derivative (**17**) quantitatively, which was further converted into **18** in 73% yield, by treatment with sodium acetate in *N*,*N*-dimethylformamide at 80 °C. Azidolysis of **18** with sodium azide in the presence of tetraethylammonium chloride in 2-methoxyethanol-water at 95°C for 18 h afforded 3-azido derivative (**19**) preferentially in 85% yield. The structure of **19** was easily determined by ^{1}H NMR spectra, where $J_{2,3}$ and $J_{3,4}$ show 10.2 and 10.4 Hz, respectively, indicating *xylo* configuration.


16 R=N_3
17 R=NH_2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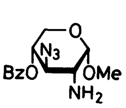
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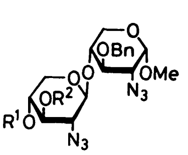
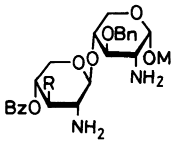
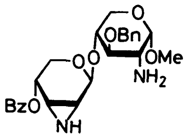
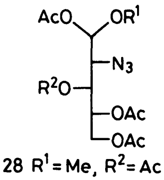
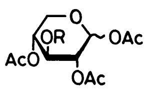

20 $R^1=R^2=H$
21 $R^1=Bz, R^2=H$
22 $R^1=H, R^2=Bz$
23 $R^1=R^2=Bz$
24 $R^1=Bz, R^2=Ms$

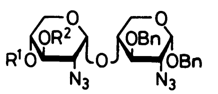

25 R = OMs
26 R = N_3

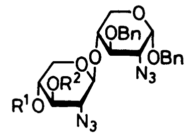

27

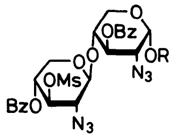
The same conversion was also substantiated in the case of disaccharide. The deacetylated derivative (**20**) of **14** was partially benzoylated with 2 molar equivalents of benzoyl chloride and triethylamine in acetone to give 4′-benzoate (**21**) in 61% yield together with 3′-benzoate (**22**) and 3′,4′-dibenzoate (**23**). The 3′-mesylate (**24**) obtained in 97% by a usual mesylation of **21** was successively hydrogenolyzed and treated with sodium acetate in the same manner as described above without any purification of the intermediate diamine (**25**) to give 2′,3′-epimino derivative (**27**) in a quantitative yield. Azidolysis of **27** with the same reagent as described above at 110 °C for 4 h give a desired isomer **26** in 63% yield. For the total synthesis of cinodine this method may assure an easy conversion of 2-azido-2-deoxy-D-xylopyranose moiety at the nonreducing end of the pseudo trisaccharide having interglycosidic ureylene linkage into 2,3-diamino-2,3-dideoxy-D-xylose moiety.

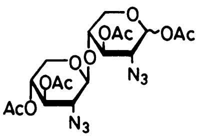

28 $R^1=Me, R^2=Ac$
29 $R^1=R^2=Bn$


30 R = Bn
31 R = Bz


32 $R^1=R^2=Ac$
33 $R^1=R^2=H$


34 $R^1=R^2=Ac$
35 $R^1=R^2=H$
36 $R^1=Bz, R^2=H$
37 $R^1=H, R^2=Bz$
38 $R^1=R^2=Bz$
39 $R^1=Bz, R^2=Ms$


40 R = Bz
41 R = Bn


42

Finally deprotection of glycoside was examined, because it is necessary for formation of the ureylene linkage. Acetolysis of the glycosides, one of the most frequently used methods, proved to be unsuccesful. Treatment of 2-azido-2-deoxy-D-xylopyranoside derivative such as methyl 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranoside (**3**) and a benzyl glycoside (**10**) with acetic anhydride in the presence of acid gave acyclic products **28** and **29**, respectively, as shown in Table 2. These results may be attributed to the retarding effect of C_2–N_3 dipole against the cleavage of C_1–OMe bond to facilitate consequently cleavage of the bond between C_1 and ring oxygen. Presence of benzyl or glycosyl substituents on the glycosyl moiety seems to have no effect on this situation. It was noteworthy that acetolysis of **3** and **10** in the presence of perchloric and trifluoroacetic acid, respectively, gave acyclic products **28** and **29** in a quantitative and 81% yields, respectively, which were obviously higher than those obtained in

Table 2. Acetolysis and Hydrolysis[a] of 2-Azido-2-deoxy-α-D-xylopyranoside Derivatives

Substrate	Acid	Concd	Solvent	Temperature °C	Time h	Product and Yield/%
3	$HClO_4$	0.18%	Ac_2O	RT	1	**28** quantitative
10	H_2SO_4	0.02%	Ac_2O/AcOH (7:3)	RT	79	**29** 34, **11** 38
10	H_2SO_4	0.05%	Ac_2O/AcOH (6:5)	RT	99	**29** 41, **11** 60
10	CF_3CO_2H	5%	Ac_2O	RT	73	**29** 81, **11** 12
8	H_2SO_4	0.5 M	70% AcOH	100	7	**7** 29, **6** 13
10	H_2SO_4	0.5 M	70% AcOH	100	4	**7** 60, **11** 35
10	H_2SO_4	0.6 M	70% AcOH	100	6	**7** 27, **6** 26, **11** 20
10	H_2SO_4	1.0 M	70% AcOH	100	2.5	**7** 53, **11** 35

a) Products were isolated after acetylation. b) 1 M=1 mol dm^{-3}.

the presence of sulfuric acid (Table 2). In the latter case, the ratio of two isomers was 3:2. Furthermore, hydrolytic deprotection of the benzyl glycoside was attempted. Benzyl glycoside (**10**) could be hydrolyzed selectively in 70% aqueous acetic acid containing 0.5—1 M (1M=1 mol dm^{-3}) sulfuric acid at 100 °C to give **7** after acetylation in good yields (Table 2). These conditions, however, proved to be not effective for selective hydrolysis of benzyl glycoside in the presence of interglycosidic linkage. For instance, the latter linkage was hydrolyzed preferentially in the case of **35**.

Finally the glycosidic linkage at the reducing end could be selectively deprotected using the benzyl glycoside as substrates by two methods. One is oxidative conversion of benzyl into benzoyl group with chromium trioxide in acetic acid.[10] This method proved to function nicely for both benzyloxy groups at C-1 and C-3 in the case of benzyl 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranoside (**4**) and 1,2,4-tri-*O*-acetyl-3-*O*-benzyl-α-D-xylopyranose (**30**),[11] respectively. Oxidation of **4** and **30** with chromium trioxide in acetic acid at room temperature gave the corresponding *O*-benzoyl derivatives **5** and **31** in 58 and 28% yields respectively. In the presence of sulfuric acid the yield for the latter increased up to 90%. The suitable disaccharide intermediate (**39**), which was derived from **35** via **36** in the same manner as described for the corresponding methyl glycoside, was oxidized by this method to give 1,3,4′-tri-*O*-benzoylated disaccharide (**40**) in 50% yield, together with small amount of selectively oxidized product (**41**). On the other hand, the second *O*-debenzylation method consists of bromination with *N*-bromosuccinimide and bromine in carbon tetrachloride followed by hydrolysis. The disaccharide **34** was converted by this method into **42** after acetylation in 56% yield. This reaction seems to be useful in a wide range of synthetic purpose and the further aspects will be published elsewhere.[12]

Experimental

General Methods. All melting points are uncorrected. The solutions were concentrated under diminished pressure at 50 °C (bath). Optical rotations were measured with a Carl Zeiss LEP-Al polarimeter. IR spectra were recorded with a Hitachi EPI-G2 grating spectrometer. ^{1}H NMR spectra were recorded with a JEOL PS-100 or a GX-400 spectrometer for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. ^{13}C NMR spectra were recorded with a JEOL FX-90 spectrometer for solutions in $CDCl_3$ unless otherwise stated. Chromatography was performed on Wakogel C-200, flash Chromatography on Wakogel C-300, and preparative TLC (PTLC) on silica gel 60 (Merck).

3,4-Di-*O*-acetyl-2-azido-1-*O*-benzoyl-2-deoxy-α-D-xylopyranose (5). To a solution of **4**[5] (114 mg, 0.33 mmol) in acetic acid (2.5 ml) was added chromium trioxide (200 mg, 2.0 mmol), and the mixture was stirred for 1 h at room temperature. The same work-up as described for **31** gave **5** in 58% yield; ^{1}H NMR δ=6.33 (d, $J_{1,2}$=3.9 Hz, H-1), 3.26 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.47 (t, $J_{3,4}$=10.5 Hz, H-3), 4.96 (dt, $J_{4,5a}$=10.5 Hz, $J_{4,5b}$=6.0 Hz, H-4), 3.65 (t, $J_{5a,5b}$=10.5 Hz, H-5a), 3.90 (dd, H-5b), 1.98 and 2.08 (each s, Ac), and 7.32—8.06 (m, Ph).

1,4-Di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxyl-D-xylopyranose (7). To a solution of **10**[5] (300 mg, 0.85 mmol) in acetic acid (72 ml) was added 0.62 M aqueous sulfuric acid (29 ml), and the solution was heated at 100 °C for 1 h. After addition of 0.93 M sulfuric acid (4.2 ml) the temperature was kept further 3 h. To the cooled solution was added sodium hydrogencarbonate (5 g), and the product was extracted 8 times with chloroform (total 80 ml). The residue obtained by evaporation of the dried extract was acetylated in a usual manner, and the product was purified on a silica-gel column with hexane-ethyl acetate (7:3) to give **7** as an anomeric mixture ($\alpha:\beta$=9:11) and **11** in 60 and 35% yields, respectively. Compound **7**: ^{1}H NMR δ=6.16 (d, $J_{1,2}$=3.0 Hz, H-1α), 3.60 (dd, H-2α), 3.94 (t, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H-3α), 4.10 (dd, $J_{4,5a}$=5.3 Hz, $J_{5a,5b}$=12.0 Hz, H-5aα), 3.56 (dd, H-5bα); 5.44 (d, $J_{1,2}$=8.0 Hz, H-1β), 3.62 (t, H-2β), 3.66 (t, $J_{2,3}$=$J_{3,4}$=9.0 Hz, H-3β), 3.93 (dd, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=11.7 Hz, H-5aβ), 3.33 (dd, $J_{4,5b}$=9.6 Hz, H-5bβ); 2.01 and 2.18 (each s, Ac), 4.72 and 4.88 (ABq, J=11.7 Hz, CH_2 in Bn), 4.73 and 4.86 (ABq, J=11.6 Hz, CH_2 in Bn), and 7.34 (s, Ph).

Found: C, 54.85; H, 5.51; N, 12.13%. Calcd for $C_{16}H_{19}N_3O_6$: C, 55.01; H, 5.48; N, 12.03%.

11: Mp 35—37 °C, $[\alpha]_D$ +85.7° (c 1.1, CH_2Cl_2), ^{1}H NMR δ=4.96 (d, $J_{1,2}$=3.0 Hz, H-1), 3.39 (dd, $J_{2,3}$=10.0 Hz, H-2), 4.04 (t, $J_{3,4}$=9.5 Hz, H-3), 5.0 (m, H-4), 3.84 (dd, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=10.5 Hz, H-5a), 3.57 (t, $J_{4,5b}$=10.5 Hz, H-5b), 1.98 (s, Ac), 4.56 and 4.79 (ABq, J=12.0 Hz, CH_2 in Bn), 4.70 and 4.87 (ABq, J=11.5 Hz, CH_2 in Bn), 7.34 and 7.39 (each s, Ph).

Found: C, 63.70; H, 5.87; N, 10.48%. Calcd for $C_{21}H_{23}N_3O_5$: C, 63.46; H, 5.83; N, 10.58%.

Methyl 2-Azido-2-deoxy-3-*O*-tetrahydropyranyl-α-D-xylo-

pyranoside (9). To a solution of methyl 2-azido-4-*O*-benzoyl-2-deoxy-α-D-xylopyranoside[5] (1.5 g, 5.1 mmol) in dry dichloromethane (40 ml) was added 3,4-dihydropyran (0.65 g, 7.7 mmol) and a solution of pyridinium *p*-toluenesulfonate (125 mg, 0.5 mmol) in dichloromethane (15 ml). The mixture was kept at room temperature for 40 h, washed with aqueous sodium chloride, dried and evaporated to give 3-*O*-tetrahydropyranyl derivative as syrup quantitatively; IR (NaCl) 2100 (azido) and 1723 cm^{-1} (ester); ^1H NMR $\delta=4.84$ (d, $J_{1,2}=3.0$ Hz, H-1), 3.26 (dd, $J_{2,3}=10.0$ Hz, H-2), 4.21 and 4.37 (each t, $J_{3,4}=10.0$ Hz, H-3), 5.14 (m, H-4), 3.63 (t, $J_{4,5a}=J_{5a,5b}=10.0$ Hz, H-5a), 3.89 (dd, $J_{4,5b}=6.0$ Hz, H-5b), 3.49 (s, OMe), 4.85 (dd, H-2 in THP), 1.2—2.0 (m, CH_2 in THP), 7.3—7.7 and 8.0—8.2 (m, Ph).

The 3-*O*-tetrahydropyranyl derivative was debenzoylated with sodium methoxide in methanol in a conventional manner to give **9** as syrup in 80% yield; IR (NaCl) 2095 cm^{-1} (azido); ^1H NMR $\delta=4.70$ (d, $J_{1,2}=3.3$ Hz, H-1), 4.62 (m, H-2 in THP), 3.41 (s, OMe) and 1.35—2.1 (m, CH_2 in THP).

Found: C, 47.95; H, 7.36; N, 15.03%. Calcd for $C_{11}H_{19}N_3O_5$: C, 48.34; H, 7.01; N, 15.38%.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranosyl)-2-azido-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (12) and Its β-(1→4) Linked Isomer (14). A. Silver Perchlorate as a Promoter: To a solution of **8** (1.5 mmol) in nitromethane (2 ml) was added silver perchlorate (0.6 mmol), 2,4,6-trimethylpyridine (0.6 mmol) and Drierite (0.9 g), and the suspension was stirred with shielding from light at −10 °C for 1 h. To this suspension was added a solution of **1**[5] (0.5 mmol) in nitromethane (2 ml) and the temperature was kept for 60 h. Undissolved materials were filtered off and washed with chloroform. The filtrate was washed with water, dried and evaporated to give a syrupy residue, which was fractionated on a silica-gel column with benzene-acetone (6 : 1) to give **12** and **14** in 33 and 40% yields, respectively.

12: Syrup, $[\alpha]_D$ +41.3° (*c* 1.0, $CHCl_3$); IR (NaCl) 2100 (azido) and 1750 (ester) cm^{-1}; ^1H NMR $\delta=4.70$ (d, $J_{1,2}=3.6$ Hz, H-1), 5.17 (d, $J_{1',2'}=3.6$ Hz, H-1′), 5.40 (dd, $J_{2',3'}=9.3$ Hz, $J_{3',4'}=10.4$ Hz, H-3′), 4.60—4.85 (m, H-4′), 3.2—4.1 (m, other ring protons), 2.04 and 2.10 (each s, Ac), 3.44 (s, OMe), 4.82 and 4.96 (ABq, $J=9.8$ Hz, CH_2 in Bn), and 7.32 (s, Ph).

Found: C, 51.20, H, 5.58; N, 15.82%. Calcd for $C_{22}H_{28}N_6O_9$: C, 50.77; H, 5.42; N, 16.15%.

14: Syrup, $[\alpha]_D$ +10.2° (*c* 1.0, $CHCl_3$); IR (NaCl) 2100 (azido) and 1750 (ester) cm^{-1}; ^1H NMR $\delta=4.67$ (d, $J_{1,2}=3.0$ Hz, H-1), 4.35 (d, $J_{1',2'}=8.1$ Hz, H-1′), 4.76—5.10 (m, H-3′ and H-4′), 3.1—4.1 (m, other ring protons), 2.03 and 2.11 (each s, Ac), 3.23 (s, OMe), 4.72 and 4.94 (ABq, $J=10.2$ Hz, CH_2 in Bn), and 7.34 (broad s, Ph).

Found: C, 50.65: H, 5.54; N, 16.46%. Calcd for $C_{22}H_{28}N_6O_9$: C, 50.77; H, 5.42; N, 16.15%.

B. Mercury(II) Cyanide as Promoter: To a solution of **1** (108 mg, 0.39 mmol) and **8**[5] (311 mg, 1.2 mmol) in dry benzene (2 ml) and nitromethane (2 ml) was added mercury(II) cyanide (240 mg, 0.88 mmol) and Drierite (0.3 g), and the mixture was stirred at 60 °C for 26 h. A similar work-up as described above and separation by preparative TLC gave **12** and **14** in 5.3 and 4.7% yields, respectively.

C. TMSOTf as a Catalyst: To a solution of **6** (104 mg, 0.38 mmol) and **8** (111 mg, 0.40 mmol) in dry 1,2-dichloroethane (2 ml) was added molecular sieve 4A (0.5 g) and TMSOTf (85 mg, 0.39 mmol) at 0 °C. The mixture was stirred at the same temperature for 24 h. Undissolved materials were filtered off and washed with chloroform. The filtrate was washed with saturated aqueous sodium hydrogencarbonate and water, dried and evaporated to give a syrupy residue, which was fractionated on PTLC to give **12** and **14** in 16 and 36% yields, respectively.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranosyl)-2-azido-2-deoxy-3-*O*-tetrahydropyranyl-α-D-xylopyranoside (13) and Its β-(1→4) Linked Isomer (15). A Silver Perchlorate as a Promoter: Compound **1** and **9** were coupled in the same manner as describe above to give **13** and **15** in 41 and 6% yields, respectively.

13: Syrup, $[\alpha]_D$ +94.0° (*c* 1.0, $CHCl_3$); IR (NaCl) 2940 (THP), 2100 (azido) and 1750 (ester) cm^{-1}; ^1H NMR $\delta=4.66$ (d, $J_{1,2}=3.2$ Hz, H-1), 3.18 (d, $J_{2,3}=9.5$ Hz, H-2), 5.43 (d, $J_{1',2'}=3.3$ Hz, H-1′), 5.38 (t, $J_{2',3'}=J_{3',4'}=9.0$ Hz, H-3′), 4.81 (m, H-4′), 3.3—4.2 (m, other ring protons), 1.3—2.0 (m, CH_2 in THP), 2.04 and 2.09 (each s, Ac), and 3.39 (s, OMe).

Found: C, 46.47; H, 6.05; N, 16.02%. Calcd for $C_{20}H_{30}N_6O_{10}$: C, 46.69; H, 5.88; N, 16.34%.

15: Syrup, $[\alpha]_D$ −8.1° (*c* 1.0, $CHCl_3$); IR (NaCl) 2930 (THP), 2105 (azido) and 1750 (ester) cm^{-1}; ^1H NMR $\delta=4.74$ (d, $J_{1,2}=3.0$ Hz, H-1), 3.28 (dd, $J_{2,3}=9.5$ Hz, H-2), 4.42 (d, $J_{1',2'}=7.8$ Hz, H-1′), 3.84—5.16 (m, H-3′ and H-4′), 3.4—4.3 (m, other ring protons), 1.3—2.0 (m, CH_2 in THP), 2.04 and 2.12 (each s, Ac), and 3.44 (s, OMe).

Found: C, 47.02; H, 5.78; N, 15.98%. Calcd for $C_{20}H_{30}N_6O_{10}$: C, 46.69; H, 5.88; N, 16.34%.

B. Silver Carbonate as a Promoter: To a solution of **9** (270 mg, 1 mmol) in dry dichloromethane (6 ml) was added silver carbonate (550 mg, 2.2 mmol), molecular sieve 4A (1 g) and **2** (480 mg, 1.5 mmol). The mixture was stirred with shielding from light for 48 h at room temperature to give only **13** in 16% yield.

C. Silver Oxide-Iodine as Promoters: To a solution of **9** (137 mg, 0.5 mmol) in dry dichloromethane (3 ml) was added silver oxide (130 mg, 0.55 mmol) and molecular sieve 4A (0.6 g). After stirring under exclusion of light for 1 h iodine (30 mg) and a solution of **2** (161 mg, 0.5 mmol) in dry dichloromethane (2 ml) were added to the mixture. After 48 h at room temperature only **13** was obtained in 10% yield.

D. Mercury(II) Oxide-Mercury(II) Bromide as Promoters: To a solution of **9** (137 mg, 0.50 mmol) in dry dichloromethane (4 ml) was added mercury(II) oxide (119 mg, 0.55 mmol) and mercury(II) bromide (6 mg, 0.02 mmol). The mixture was stirred at room temperature with shielding from light for 30 min, and solution of **2** (161 mg, 0.50 mmol) was added. After 48 h at room temperature only **13** was obtained in 11% yields.

Methyl 2-Azido-4-*O*-benzoyl-2-deoxy-3-*O*-methylsulfonyl-α-D-xylopyranoside (16). Methyl 2-azido-4-*O*-benzoyl-2-deoxy-α-D-xylopyranoside[5] was treated with methanesulfonyl chloride in pyridine in a usual manner to give **16** in 85% yield, mp 53—54 °C, $[\alpha]_D$ −79.1° (*c* 1.0, $CHCl_3$); ^1H NMR $\delta=4.90$ (d, $J_{1,2}=3.5$ Hz, H-1), 3.41 (dd, $J_{2,3}=9.6$ Hz, H-2), 5.08—5.36 (m, H-3 and H-4), 4.01 (dd, $J_{4,5a}=5.2$ Hz, $J_{5a,5b}=10.6$ Hz, H-5a), 3.66 (dd, $J_{4,5b}=9.3$ Hz, H-5b), 3.04 (s, Ms), 3.47 (s, OMe), and 7.26—7.63 and 8.00—8.16 (m, Ph).

Found: C, 45.33; H, 4.51; N, 11.16; S, 8.85%. Calcd for $C_{14}H_{17}N_3O_7S$: C, 45.28; H, 4.61; N, 11.32; S, 8.63%.

Methyl 2-Amino-3-azido-4-*O*-benzoyl-2,3-dideoxy-α-D-xylopyranoside (19). To a solution of **16** (0.2 mmol) in methanol (10 ml) was added platinum oxide (11 mg) and then introduced hydrogen until compound **16** disappeared on TLC. The catalyst was filtered off and the filtrate was evaporated to give **17** quantitatively. To a solution of **17** in *N*,*N*-dimethylformamide-water (5:1, 2ml) was added sodium acetate trihydrate (122 mg). The solution was heated at 80 °C for 3 h, and evaporated to give a residue. Acetone was added to the residue and undissolved materials were filtered off. The filtrate was evaporated to give a syrup, which was purified on PTLC to give **18** in 73% yield; ^{1}H NMR $\delta=4.82$ (d, $J_{1,2}=3.4$ Hz, H-1), 2.63 (dd, $J_{2,3}=5.9$ Hz, H-2), 2.79 (dd, $J_{3,4}=3.9$ Hz, H-3), 5.26 (ddd, $J_{4,5a}=5.5$ Hz, $J_{4,5b}=7.3$ Hz, H-4), 3.58 (dd, $J_{5a,5b}=11.7$ Hz, H-5a), 3.80 (dd, H-5b), 1.94 (NH), 3.45 (s, OMe), 7.20—7.60 and 7.95—8.10 (m, Ph).

To a solution of the epimino sugar **18** (0.5 mmol) in 2-methoxyethanol-water (14:1, 5 ml) was added sodium azide (2.5 mmol) and ammonium chloride (2.5 mmol). The mixture was heated at 95 °C for 18 h, and evaporated to give a residue. Acetone was added to the residue and undissolved materials were filtered off. The filtrate was evaporated to give a syrup, which was purified on PTLC to give **19** in 85% yield. This compound was characterized only by the following ^{1}H NMR data: $\delta=4.67$ (d, $J_{1,2}=3.3$ Hz, H-1), 2.74 (dd, $J_{2,3}=10.2$ Hz, H-2), 3.59 (t, $J_{3,4}=10.4$ Hz, H-3), 5.00 (dt, $J_{4,5a}=10.4$ Hz, $J_{4,5b}=5.4$ Hz, H-4), 3.66 (t, $J_{5a,5b}=10.4$ Hz, H-5a), 3.94 (dd, H-5b), 2.02 (NH), 3.42 (s, OMe), 7.30—7.65 and 7.95—8.12 (m, Ph).

Methyl 2-Azido-4-*O*-(2-azido-2-deoxy-*β*-D-xylopyranosyl)-3-*O*-benzyl-2-deoxy-*α*-D-xylopyranoside (20). Deacetylation of **14** with sodium methoxide in methanol in a usual manner gave **20** quantitatively, $[\alpha]_D$ +41.3° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=4.76$ (d, $J_{1,2}=3.3$ Hz, H-1), 4.36 (d, $J_{1',2'}=7.5$ Hz, H-1′), 3.1—4.1 (m, other ring protons) 3.48 (s, OMe), 4.80 and 5.03 (ABq, $J=10.2$ Hz, CH$_2$ in Bn), and 7.35—7.60 (m, Ph).

Found: C, 49.54; H, 5.56; N, 19.24%. Calcd for $C_{18}H_{24}N_6O_7$: C, 49.53; H, 5.54; N, 19.26%.

Partial Benzoylation of 20. To a solution of **20** (860 mg, 2.00 mmol) in acetone (8 ml) was added at 0 °C triethylamine (0.8 ml, 5.8 mmol) and benzoyl chloride (0.46 ml, 3.5 mmol), and the mixture was kept at room temperature for 18 h. After addition of water (2 ml) the mixture was stirred for 2 h, diluted with chloroform (30 ml), washed with water, dried and evaporated to give a mixture of three components, which was fractionated on a silica-gel column with benzene-acetone (30:1) to give **21**, **22**, and **23** in 61, 5, and 32% yields, respectively.

21: MP 118—122 °C, $[\alpha]_D$ −80° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=4.68$ (d, $J_{1,2}=3.6$ Hz, H-1), 4.36 (d, $J_{1',2'}=7.4$ Hz, H-1′), 5.05 (dt, $J_{3',4'}=J_{4',5'a}=9.0$ Hz, $J_{4',5'b}=5.5$ Hz, H-4′), 4.14 (dd, $J_{5'a,5'b}=11.6$ Hz, H-5′b), 3.18—4.00 (m, other ring protons), 3.43 (s, OMe), 4.76 and 4.96 (ABq, $J=10.2$ Hz, CH$_2$ in Bn), 7.35 (s, Ph in Bn), and 7.24—7.66 and 7.93—8.08 (m, Ph in Bz).

Found: C, 56.01; H, 5.31; N, 15.79%. Calcd for $C_{25}H_{28}N_6O_8$: C, 55.55; H, 5.22; N, 15.55%.

22: Syrup, $[\alpha]_D$ +19.7° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=4.69$ (d, $J_{1,2}=3.2$ Hz, H-1), 4.43 (d, $J_{1',2'}=7.5$ Hz, H-1′), 4.87 (dd, H-3′), 3.2—4.1 (m, other ring protons), 3.43 (s, OMe), 4.75 and 4.98 (ABq, $J=11.7$ Hz, CH$_2$ in Bn), 7.25—7.45 and 8.00—8.10 (m, Ph).

Found: C, 55.61; H, 5.29; N, 15.73%. Calcd for $C_{25}H_{28}N_6O_8$: C, 55.55; H, 5.22; N, 15.55%.

23: Syrup, $[\alpha]_D$ −61.2° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=4.72$ (s, $J_{1,2}=4.5$ Hz, H-1), 4.59 (d, $J_{1',2'}=7.5$ Hz, H-1′), 5.49 (t, $J_{2',3'}=J_{3',4'}=8.4$ Hz, H-3′), 5.14 (dt, $J_{4',5'a}=8.4$ Hz, $J_{4',5'b}=5.4$ Hz, H-4′), 4.28 (dd, $J_{5'a,5'b}=11.4$ Hz, H-5′b), 3.18—4.04 (m, other ring protons), 3.47 (s, OMe), 4.80 and 5.02 (ABq, $J=9.6$ Hz, CH$_2$ in Bn), and 7.24—7.60 and 7.94—8.06 (m, Ph).

Found: C, 59.14; H, 5.00; N, 13.28%. Calcd for $C_{32}H_{32}N_6O_9$: C, 59.62; H, 5.00; N, 13.04%.

Methyl 2-Azido-4-*O*-(2-azido-4-*O*-benzoyl-2-deoxy-3-*O*-methylsulfonyl-*β*-D-xylopyranosyl)-3-*O*-benzoyl-2-deoxy-*α*-D-xylopyranoside (24). Treatment of **21** with methanesulfonyl chloride in pyridine in a usual manner gave **24** in 97% yield, mp 128—130 °C, $[\alpha]_D$ −32.3° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=4.53$ (d, $J_{1,2}=1.5$ Hz, H-1), 4.45 (d, $J_{1',2'}=7.7$ Hz, H-1′), 4.53 (dd, $J_{2',3'}=9.8$ Hz, $J_{3',4'}=9.0$ Hz, H-3′), 5.10 (dt, $J_{4',5'a}=9.0$ Hz, $J_{4',5'b}=5.1$ Hz, H-4′), 4.26 (dd, $J_{5'a,5'b}=12.0$ Hz, H-5′b), 3.16—4.02 (m, other ring protons), 3.08 (s, Ms), 4.80 and 4.95 (ABq, $J=10.2$ Hz, CH$_2$ in Bn), and 7.28—7.64 and 7.98—8.16 (m, Ph).

Found: C, 50.42; H, 4.81; N, 13.55; S, 5.21%. Calcd for $C_{26}H_{30}N_6O_{10}S$: C, 50.48; H, 4.89; N, 13.59; S, 5.18%.

Methyl 2-Amino-4-*O*-(2-amino-3-azido-4-*O*-benzoyl-2,3-dideoxy-*β*-D-xylopyranosyl)-3-*O*-benzyl-2-deoxy-*α*-D-xylopyranoside (26). Azidolysis of **27** was carried out in the same manner as described for **19** to give **26** as a syrup in 63% yield, $[\alpha]_D$ −7.7° (c 1.0, CHCl$_3$); IR (NaCl) 3370 and 3300 (NH$_2$), 2100 (azido), and 1725 (ester) cm^{-1}; ^{1}H NMR $\delta=4.65$ (d, $J_{1,2}=1.5$ Hz, H-1), 4.31 (d, $J_{1',2'}=7.5$ Hz, H-1′), 2.75 (dd, $J_{2',3'}=10.2$ Hz, H-2′), 5.10 (m, H-4′), 3.39 (s, OMe), and 7.28—8.16 (m, Ph).

Found: C, 57.93; H, 6.09; N, 13.29%. Calcd for $C_{25}H_{31}N_5O_7$: C, 58.47; H, 6.08; N, 13.64%.

Methyl 2-Amino-4-*O*-(4-*O*-benzoyl-2,3-dideoxy-2,3-epimino-*β*-D-ribopyranosyl)-3-*O*-benzyl-*α*-D-xylopyranoside (27). Hydrogenolysis of **24** in dichloromethane in the presence of platinum oxide in the same manner as described for **19** gave **25** quantitatively; ^{1}H NMR $\delta=4.66$ (d, $J_{1,2}=3.2$ Hz, H-1), 2.80 (dd, $J_{2,3}=9.2$ Hz, H-2), 4.34 (d, $J_{1',2'}=7.5$ Hz, H-1′), 3.01 (dd, $J_{2',3'}=9.3$ Hz, H-2′), 3.80 (t, $J_{3',4'}=9.3$ Hz, H-3′), 5.22 (dt, $J_{4',5'a}=9.3$ Hz, $J_{4',5'b}=6.0$ Hz, H-4′), 4.27 (dd, $J_{5'a,5'b}=12.0$ Hz, H-5′b), 3.11—3.96 (m, other ring protons), 2.10 (NH), 3.01 (s, Ms), 3.40 (s, OMe), 4.62 and 5.00 (ABq, $J=11.3$ Hz, CH$_2$ in Bn), and 7.28—7.64 and 8.00—8.16 (m, Ph).

Treatment of **25** with sodium acetate in the same manner as described for **19** gave **27** as a syrup in 90% yield, $[\alpha]_D$ +47.9° (c 1.0, CHCl$_3$); IR (NaCl) 3360 and 3275 (OH and NH$_2$), and 1708 (ester) cm^{-1}; ^{1}H NMR (after D$_2$O exchange) $\delta=4.66$ (d, $J_{1,2}=3.0$ Hz, H-1), 5.07 (s, H-1′), 2.30 (d, $J_{2',3'}=5.0$ Hz, H-2′), 2.8 (m, H-2 and H-3′), 4.96—5.14 (m, H-4′), 3.44—4.20 (m, other ring protons), 3.43 (s, OMe), 4.72 and 4.89 (ABq, $J=11.4$ Hz, CH$_2$ in Bn), 7.34 (s, Ph in Bn), and 7.26—7.62 and 7.96—8.14 (m, Bz).

Found: C, 63.53; H, 6.51; N, 5.66%. Calcd for $C_{25}H_{30}N_2O_7$: C, 63.82; H, 6.43; N, 5.95%.

1,3,4,5-Tetra-*O*-acetyl-2-azido-2-deoxy-D-xylose Methyl Hemiacetal (28). To a solution of **3**5) (167 mg, 0.61 mmol) in acetic anhydride (1 ml) was added acetic anhydride (2 ml) containing one drop of 60% perchloric acid.

The mixture was kept at room temperature for 1 h, poured into saturated aqueous sodium hydrogencarbonate, and extracted with chloroform. The extract was washed with water, dried and evaporated to give **28** as a syrup quantitatively, $[\alpha]_D$ +21.2° (c 1.0, CHCl$_3$); ^{1}H NMR $\delta=5.74$ (d, $J_{1,2}=5.9$ Hz, H-1), 3.67 (dd, $J_{2,3}=3.0$ Hz, H-2), 5.12—5.48 (m, H-3 and H-4), 3.98—4.44 (m, H-5a and H-5b), 3.51 (s, OMe) and 2.12 and 2.14 (Ac).

Found: C, 44.73; H, 5.57; N, 11.00%. Calcd for $C_{14}H_{21}N_3O_9$: C, 44.80; H, 5.64; N, 11.20%.

1,4,5-Tri-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-D-xylose Benzyl Hemiacetal (29). To a chilled solution of **10**[5] (58 mg, 0.16 mmol) in acetic anhydride (6 ml) was added trifluoroacetic acid (0.3 ml). The solution was kept at room temperature for 73 h and poured into saturated aqueous sodium hydrogencarbonate. Chloroform extract was washed with water, dried and evaporated to give a syrupy residue, which was purified on a silica-gel column with hexane-ethyl acetate (4:1) to give **29** in 81% yield. In its ^{1}H NMR spectrum signals due to two epimers were observed with a ratio of 3:2. ^{1}H NMR (400 MHz) major component δ=6.13 (d, $J_{1,2}$=6.8 Hz, H-1), 3.53 (dd, $J_{2,3}$=3.2 Hz, H-2), 3.98 (dd, $J_{3,4}$=6.2 Hz, H-3), 5.37 (dq, $J_{4,5a}$=7.0 Hz, $J_{4,5b}$=3.2 Hz, H-4), 4.20 (t, $J_{5a,5b}$=8.0 Hz, H-5a), 4.39 (dd, H-5b); Minor component δ=6.07 (d, $J_{1,2}$=5.4 Hz, H-1), 3.79 (t, $J_{2,3}$=4.2 Hz, H-2), 3.86 (t, $J_{3,4}$=4.4 Hz, H-3), 5.28 (dq, $J_{4,5a}$=7.0 Hz, $J_{4,5b}$=5.0 Hz, H-4), 4.17 (t, $J_{5a,5b}$=7.6 Hz, H-5a), 4.36 (dd, H-5b); 1.90—2.07 (m, Ac), 4.36—4.79 (m, CH_2 in Bn), and 7.20—7.40 (m, Ph).

Found: C, 59.79; H, 5.80; N, 8.19%. Calcd for $C_{25}H_{29}N_3O_8$: C, 60.11; H, 5.85; N, 8.41%.

1,2,4-Tri-*O*-acetyl-3-*O*-benzoyl-α-D-xylopyranose (31). To a mixture of acetic acid (2.5 ml) and acetic anhydride (0.2 ml) was added one drop of concd sulfuric acid, chromium trioxide (276 mg, 2.8 mmol) and **30**[10] (186 mg, 0.51 mmol). The mixture was kept at room temperature for 1 h, diluted with chloroform, and washed successively with water, aqueous sodium hydrogencarbonate, and water. The solution was dried and evaporated to give a syrup residue, which was purified on PTLC with hexane–ethyl acetate (7:3) to give **31** in 90% yield, $[\alpha]_D$ +48.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=6.29 (d, $J_{1,2}$=3.3 Hz, H-1),5.21 (dd, $J_{2,3}$= 9.8 Hz, H-2), 5.74 (t, $J_{3,4}$=9.8 Hz, H-3), 5.2 (m, H-4), 3.79 (t, $J_{4,5a}$=$J_{5a,5b}$=10.8 Hz, H-5a), 4.00 (dd, $J_{4,5b}$=6.0 Hz, H-5b), 1.93, 1.97 and 2.21 (each s, Ac), and 7.32—7.66 and 7.92—8.06 (m, Ph).

Found: C, 56.23; H, 5.08%. Calcd for $C_{18}H_{20}O_9$: C, 56.84; H, 5.30%.

Benzyl 2-Azido-4-*O*-(2-azido-2-deoxy-α-D-xylopyranosyl)-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (33) and Its β-Linked Isomer (35). Compounds **1** (1.51 g, 5.44 mmol) and **10** (3.80 g, 10.4 mmol) were coupled in the same manner as described for the preparation of **12** and **14** (Method A) to give a mixture of **32** and **34**, which was separated, after deacetylation with sodium methoxide in methanol, on a silica-gel column with benzene-acetone (6:1) to give **33** and **35** in 29 and 46% yields, respectively.

33: Syrup, $[\alpha]_D$ +88.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.92 (d, $J_{1,2}$=3.6 Hz, H-1), 3.36 (dd, $J_{2,3}$=9.8 Hz, H-2), 5.18 (d, $J_{1',2'}$=4.0 Hz, H-1'), 3.25 (dd, $J_{2',3'}$=10.2 Hz, H-2'), 3.48—4.10 (m, other ring protons), 4.32 (s, OH×2), 4.60 and 4.82 (ABq, J=11.7 Hz, CH_2 in Bn), 4.88 and 5.10 (ABq, J=9.9 Hz, CH_2 in Bn), and 7.48 (broad s, Ph).

Found: C, 56.43; H, 5.59; N, 16.27%. Calcd for $C_{24}H_{28}N_6O_7$: C, 56.24; H, 5.51; N, 16.40%.

^{1}H NMR data of 3',4'-diacetate (**32**): δ=4.93 (d, $J_{1,2}$=2.5 Hz, H-1), 4.38 (d, $J_{1',2'}$=8.0 Hz, H-1'), 4.53 and 4.75 (ABq, J=12.5 Hz, CH_2 in Bn), 4.85 and 4.97 (ABq, J=10.0 Hz, CH_2 in Bn), 2.03 and 2.11 (each s, Ac), and 7.35 (s, Ph).

35: Syrup, $[\alpha]_D$ +68.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.94 (d, $J_{1,2}$=3.6 Hz, H-1), 3.17 (dd, $J_{2,3}$=10.5 Hz, H-2), 4.34 (d, H-1').

Found: C, 55.88; H, 5.59; N, 15.99%. Calcd for $C_{24}H_{28}N_6O_7$: C, 56.24; H, 5.51; N, 16.40%.

^{1}H NMR data of 3',4'-diacetate (**34**): δ=4.90 (d, $J_{1,2}$=4.0 Hz, H-1), 3.35 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.18 (d, $J_{1',2'}$=3.5 Hz, H-1'), 3.27 (dd, $J_{2',3'}$=10.0 Hz, H-2'), 5.46 (t, $J_{3',4'}$=8.5 Hz, H-3'), 4.51 and 4.77 (ABq, J=12.5 Hz, CH_2 in Bn), 4.87 and 5.03 (ABq, J=10.0 Hz, CH_2 in Bn), 2.00 and 2.07 (each s, Ac), and 7.38 (s, Ph).

Partial Benzoylation of 35. Treatment of **35** (1.80 g, 3.5 mmol) with benzoyl chloride (0.69 ml, 6.0 mmol) and triethylamine (1.4 ml, 10 mmol) in acetone (20 ml) in the same manner as described in the partial benzoylation of **21** gave, by separation on a silica-gel column with benzene-acetone (40:1), 4'-benzoate (**36**), 3'-benzoate (**37**), and 3'4'-dibenzoate (**38**) in 67, 13, and 17% yields, respectively.

36: Syrup, $[\alpha]_D$ +8.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.96 (d, $J_{1,2}$=3.3 Hz, H-1), 4.45 (d, $J_{1',2'}$=7.6 Hz, H-1'), 5.15 (dt, $J_{3',4'}$=$J_{4',5'a}$=9.8 Hz, $J_{4',5'b}$=5.3 Hz, H-4'), 4.22 (dd, $J_{5a,5b}$=12.0 Hz, H-5'b), 3.24—4.10 (m, other ring protons), 4.61 and 4.83 (ABq, J=12.3 Hz, CH_2 in Bn), 4.85 and 5.06 (ABq, J=10.5 Hz, CH_2 in Bn), 7.46 (s, Ph in Bn), and 7.34—7.74 and 8.04—8.20 (m, Bz).

Found: C, 60.56; H, 5.16; N, 13.41%. Calcd for $C_{31}H_{32}N_6O_8$: C, 60.38; H, 5.23; N, 13.63%.

37: Syrup, $[\alpha]_D$ +30.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.95 (d, $J_{1,2}$=3.4 Hz, H-1), 4.50 (d, $J_{1',2'}$=8.1 Hz, H-1'), 3.56 (dd, $J_{2',3'}$=9.9 Hz, H-2'), 5.03 (t, H-3'), 3.17—3.45 (m, H-2 and H-4'), 3.75—4.20 (m, other ring protons), 4.60 and 4.82 (ABq, J=12.0 Hz, CH_2 in Bn), 4.86 and 5.08 (ABq, J=10.5 Hz, CH_2 in Bn), 7.45 (s, Ph in Bn), and 7.35—7.80 and 8.13—8.27 (m, Bz).

Found: C, 60.07; H, 5.35; N, 13.41%. Calcd for $C_{31}H_{32}N_6O_8$: C, 60.38; H, 5.23; N, 13.63%.

38: Syrup, $[\alpha]_D$ −28.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.97 (d, $J_{1,2}$=3.8Hz, H-1), 4.60(d, $J_{1',2'}$=7.7 Hz, H-1'), 5.55 (t, $J_{2',3'}$=$J_{3',4'}$=9.0 Hz, H-3'), 5.36 (dt, $J_{4',5'a}$=9.0 Hz, $J_{4',5'b}$=5.7 Hz, H-4'), 4.35 (dd, $J_{5'a,5'b}$=12.0 Hz, H-5'b), 3.32—4.16 (m, other ring protons), 4.62 and 4.82 (ABq, J=13.0 Hz, CH_2 in Bn), 4.86 and 5.09 (ABq, J=10.5 Hz, CH_2 in Bn), 7.45 (s, Ph in Bn), 7.35—7.70 and 7.96—8.20 (m, Bz).

Found: C, 63.21; H, 5.01; N, 11.93%. Calcd for $C_{38}H_{36}N_6O_9$: C, 63.33; H, 5.04; N, 11.66%.

Benzyl 2-Azido-4-*O*-(2-azido-4-*O*-benzyl-2-deoxy-3-*O*-methylsulfonyl-β-D-xylopyranosyl)-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (39). Methylsulfonylation of **36** in a usual manner gave **39** as a syrup quantitatively, $[\alpha]_D$ −10.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.96 (d, $J_{1,2}$=3.3 Hz, H-1), 3.25 (H-2), 4.50 (d, $J_{1',2'}$=8.3 Hz, H-1'), 3.56 (dd, $J_{2',3'}$=10.2 Hz, H-2'), 4.78 (t, $J_{3',4'}$=9.8 Hz, H-3'), 5.25 (dt, $J_{4',5'a}$=9.8 Hz, $J_{4,5'b}$=5.7 Hz, H-4'), 3.29 (dd, $J_{5'a,5'b}$=12.0 Hz, H-5'a), 4.29 (dd, H-5'b), 3.7—4.1 (m, other ring protons), 3.03 (s, Ms), 4.62 and 4.82 (ABq, J=12.0 Hz, CH_2 in Bn), 4.84 and 5.01 (ABq, J=10.8 Hz, CH_2 in Bn), 7.43 (s, Ph in Bn), and 7.32—7.66 and 8.0—8.22 (m, Bz).

Found: C, 55.27; H, 4.90; N, 11.81; S, 4.63%. Calcd for $C_{32}H_{34}N_6O_{10}S$: C, 55.32; H, 4.93; N, 12.10; S, 4.63%.

2-Azido-4-*O*-(2-azido-4-*O*-benzyl-2-deoxy-3-*O*-methylsulfonyl-β-D-xylopyranosyl)-1,3-di-*O*-benzoyl-2-deoxy-α-D-xylopyranose (40). Compound **39** was oxidized in the same manner as described for **32** to give **40** in 50% yield, $[\alpha]_D$ +24.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=6.57 (d, $J_{1,2}$=3.6 Hz, H-1), 3.81 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.94 (dd, $J_{3,4}$=8.3 Hz, H-3), 4.49 (d, $J_{1',2'}$=7.5 Hz, H-1'), 3.56 (dd, $J_{2',3'}$=10.2 Hz, H-2'), 4.69 (dd,

$J_{3',4'}$=9.8 Hz, H-3'), 5.04 (dt, $J_{4',5'a}$=9.8 Hz, $J_{4',5'b}$=5.3 Hz, H-4'), 3.5—4.3 (m, other ring protons), 3.05 (s, Ms), and 7.37—7.80 and 8.04—8.32 (m, Bz).

Found: C, 53.30; H, 4.30; N, 11.43; S, 4.71%. Calcd for $C_{32}H_{30}N_6O_{12}S$: C, 53.18; H, 4.18; N, 11.63; S, 4.44%.

A partially oxidized product **41** was also obtained in 7% yield, mp 172—8 °C (decomp), $[\alpha]_D$ +11.3° (*c* 1.0 $CHCl_3$); ^1H NMR δ=5.10 (d, $J_{1,2}$=3.6 Hz, H-1), 3.32 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.84 (dd, $J_{3,4}$=8.5 Hz, H-3), 4.45 (d, $J_{1',2'}$=7.5 Hz, H-1'), 3.53 (dd, $J_{2',3'}$=9.9 Hz, H-2'), 4.67 (t, $J_{3',4'}$=9.9 Hz, H-3'), 4.98 (m, H-4'), 3.63—4.20 (m, other ring protons), 3.05 (s, Ms), 4.69 and 4.89 (ABq, *J*=12.3 Hz, CH_2 in Bn), 7.48 (broad s, Ph in Bn), and 7.36—7.70 and 8.04—8.26 (m, Bz).

Found: C, 54.63; H, 4.60; N, 11.76; S, 4.48%. Calcd for $C_{32}H_{32}N_6O_{11}S$: C, 54.23; H, 4.55; N, 11.86; S, 4.52%.

1,3-Di-*O*-acetyl-4-*O*-(3,4-di-*O*-acetyl-2-azido-2-deoxy-*β*-D-xylopyranosyl)-2-azido-2-deoxy-D-xylopyranose (42). To a solution of **34** (50 mg, 0.084 mmol) in carbon tetrachloride (4.2 ml) was added with stirring *N*-bromosuccinimide (33 mg, 0.19 mmol) and a catalytic amount of bromine, and the mixture was kept at room temperature for 24 h. After a developed red color faded, undissolved materials were filtered off and washed with chloroform (5 ml). The filtrate was mixed with a solution of sodium hydrogencarbonate (0.05 g) in water (1 ml), stirred at room temperature for 2 h, and evaporated. The residue was acetylated in a conventional manner and fractionated on a silica-gel column with hexane–ethyl acetate (7 : 3) to give **42** (23 mg, 56%) as an anomeric mixture ($\alpha:\beta$=2 : 3); ^1H NMR δ=6.15 (d, $J_{1,2}$=3.5 Hz, H-1α), 5.46 (d, $J_{1,2}$=8.0 Hz, H-1β), 4.30 (d, $J_{1',2'}$=7.5 Hz, H-1'), and 2.02—2.18 (many s, 12 H, Ac).

Found: C, 43.55; H, 4.93; N, 16.55%. Calcd for $C_{18}H_{24}N_6O_{11}$: C, 43.20; H, 4.83; N, 16.80%.

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