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Preparation of 2-Azido-2-deoxypentose Derivatives

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2-Azido-2-deoxypentose derivatives having D-*xylo* and L-*arabino* configurations were prepared via azidonitration of 1,5-anhydro-2-deoxypent-1-enitols, that is, xylal and arabinal derivatives, respectively. The L-*ribo* isomer was prepared by substitution of 2-trifluoromethylsulfonyloxy and 2-(1-imidazolylsulfonyloxy) group with azide. The D-*xylo* isomer was converted into the corresponding D-*ribo* and D-*lyxo* isomers.

Recently 2-amino-2-deoxypentoses were reported as components of antibiotics such as glycocinnamoylspermidines (cinodine)[1] as well as adenine nucleosides[2] isolated from bacterial metabolites. On the other hand, 2-azido sugars have been used by preference on the occasion of synthesis of biologically important oligosaccharides[3] as a precursor of 2-amino sugars which are bonded through 1,2-cis glycosidic linkage. We have studied preparation of 2-azido-2-deoxypentoses as a part of total synthesis of cinodine which had an α-ureylene linkage through 2-amino-2-deoxy-D-xylose, while very recently this linkage was revised to be β in the course of structure elucidation of a closely related antibiotic, glycocinnasperimicin D.[4]

For the introduction of azido group the ring-opening reaction of epoxy derivatives and the substitution reaction have been used as the conventional methods. In the case of 2-azido-2-deoxypentopyranoside, however, both methods encounter synthetic difficulties. In the former, the conformational flexibility of pentopyransosides leads to lose the stereoelectronic control of the ring-opening reaction, that is, the reaction does not obey the Fürst-Plattner rule any more,[5] while in the latter the substitution at C-2 carbon are retarded by the neighboring anomeric center which has two polar carbon-oxygen bonds.[6] In this paper 2-azido-2-deoxypentopyranosides having D-*xylo* (and D-*lyxo* as minor component) and L-*arabino* configurations were prepared by the azidonitration method[7] and L-*ribo* isomer by substitution reaction of the reactive 2-*O*-sulfonyl derivatives with azide. Furthermore, D-*ribo* and L-*lyxo* isomers were derived from the D-*xylo* isomer by inversion of hydroxyl groups via the corresponding 3-ulose and 3,4-anhydro derivative, respectively.

Results and Discussion

Although the azidonitration of 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*threo*-pent-1-enitol (D-xylal diacetate, **1**) was first reported by Lemieux and Ratcliffe,[7] they reported only the ratio of D-*xylo* and D-*lyxo* isomers as 2:1. In this paper the isomer ratio was roughly estimated from the isolated yields after conversion into 1-acetates or methyl glycosides. For the former conversion once isolated and crude mixture of azidonitrates was acetylated with acetic anhydride and sodium acetate at 70 °C. For the latter methanol was added directly to the reaction solution of azidonitration. Methyl glycosides were obtained in higher yields than 1-acetates as shown in Table. In the case of **1**, it seems that the reaction temperature is one of the important factors controlling the ratio of two isomers (**3**/**6** or **4**/**7**) as reported for the azidonitration of D-glucal triacetate.[8] While at −10—−15 °C the ratio was about 2—3, at the lower temperature, albeit with higher molar ratios of cerium(IV) ammonium nitrate and sodium azide, the ratio increased to 12. However, more detailed experiments should be necessary for definitive explanation of the stereoselectivity. Thus,

Table 1. Azidonitration of 3,4-Di-*O*-acetyl-2-deoxy-D-*threo*-pent-1-enitol (**1**) and Its L-*Erythro* Isomer (**2**)

Glycal	Molar ratio[a]		Atmosphere	Temperature	Product	Ratio
	CAN[b]	NaN_3		°C	Yield/%	(eq-N_3/ax-N_3)[c]
1	2.0	1.1	N_2	−10	**3**(43), **6**(13)	3.3
1	2.0	1.5	N_2	−12	**3**(38), **6**(16)	2.4
1	2.0	5.2	N_2	−12	**3**(23), **6**(16)	1.4
1	3.0	1.1	N_2	−12	**3**(43), **6**(13)	3.3
1	3.0	1.5	N_2	−10	**3**(47), **6**(14)	3.4
1	2.0	1.5	air	−15	**3**(27), **6**(8)	3.3
1	4.3	2.3	air	−20	**3**(58), **6**(5)	12
1	4.0	2.0	air	−20	**4**(84), **7**[d]	>15
2	3.0	1.5	air	−10	**8**(55, α/β=1.8)	e)

a) Glycal=1.0. b) Cerium(IV) ammonium nitrate. c) eq=equatorial; ax=axial. d) Less than 5%. e) The product with ax-N_3 group colud not be isolated.

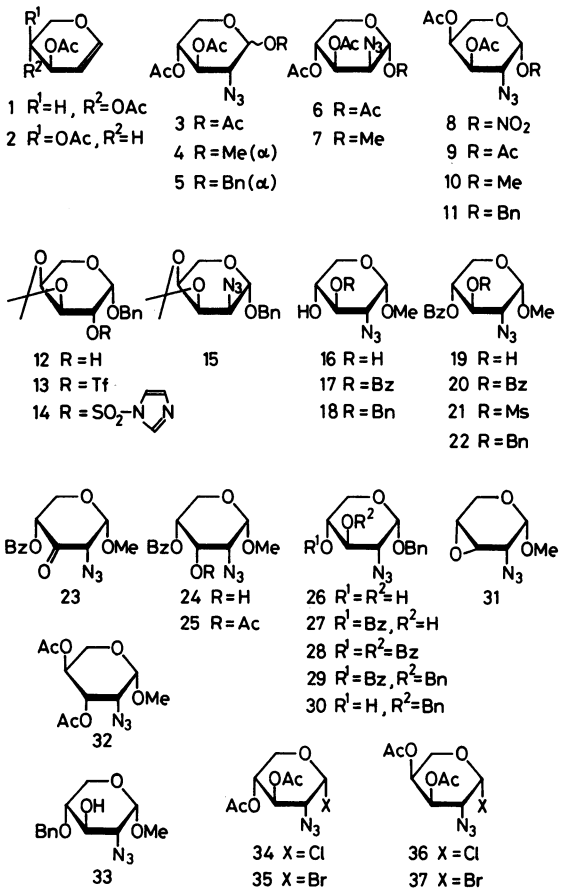
the reaction could be carried out even under aerobic conditions at −20 °C, for instance, to give **4** almost selectively in 84% yield, where the *lyxo* isomer (**7**) was obtained in trace amount.

On the other hand, the azidonitration of 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-L-*erythro*-pent-1-enitol (L-arabinal diacetate, **2**), proceeded stereoselectively even at −10 °C to give D-*arabino* isomer (**9** or **10**) in a similar manner as D-galactal triacetate.[7] In this case the β-anomer of azidonitrate **8** could be isolated as crystals in 52% yield. The stereoselectivity can be explained by the steric hindrance of axially oriented 4-acetoxyl group in the half-chair conformation to favor the attack of azide radical from its opposite site.

The corresponding benzyl glycosides (**5** and **11**) were prepared by treatment of the azido nitrates with benzyl alcohol. The yield of **5** was 55% including the azidonitration step, while that of **11** from the nitrate **8** was 90%. Thus *xylo* and *arabino* isomers of 2-azido-2-deoxypentopyranose derivatives could be prepared by azidonitration method, and the remaining *ribo* and *lyxo* isomers was planned to be derived by different methods.

Preparation of 2-azido-2-deoxyribopyranosides was achieved by two methods. In the first method benzyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside (**12**) was used as an easily-available starting compound and converted into the 2-triflate (**13**) and 2-(1-imidazolesulfonate) (**14**), which are the derivatives of choice often used for the retarded substitution reaction.[9] Treatment of **13** and **14** with sodium azide gave the corresponding 2-azido derivative (**15**) in 27% (2 steps) and 80% yields, respectively. In the second method the configuration on C-3 of D-*xylo* isomer was inverted by oxidation and successive reduction. The deacetylated derivative (**16**) of **4** was benzoylated with benzoyl chloride and triethylamine in acetone at room temperature to give 3-benzoate (**17**), 4-benzoate (**19**), and 3,4-dibenzoate (**20**) in 5, 65, and 29% yields, respectively. Oxidation of **19** with dimethyl sulfoxide and trifluoroacetic anhydride followed by reduction of the resulting 3-ulose (**23**) with sodium borohydride afforded in 75% yield an another *ribo* isomer (**24**), which was further characterized as the 3-acetate (**25**). The corresponding benzyl glycoside derivatives (**26**—**28**) were prepared in a similar manner as described for the methyl glycosides (**16**, **19**, and **20**).

The remaining isomer of 2-azido-2-deoxypentose, that is, *lyxo* isomer could be also derived from the *xylo* isomer. The 3-mesylate (**21**) of **19** was treated with potassium hydroxide in methanol gave the 3,4-anhydro derivative (**31**) in 76% yield. Treatment of **31** with sodium acetate and acetic acid in *N*,*N*-dimethylformamide at 100 °C, followed by acetylation, gave the desired L-*lyxo* isomer (**32**) predominantly in 54% yield together with the D-*xylo* isomer **4** in 25% yield. Thus facile preparative methods of all stereoisomers of 2-azido-2-deoxypentose could be established.



Furthermore, some *O*-benzyl derivatives and glycosyl halides were also prepared. Methyl 2-azido-3-*O*-benzyl-2-deoxy-D-xylopyranoside (**18**) were easily derived via **22** in 74% yield, by treatment of **19** with benzyl bromide and silver oxide followed by debenzoylation. The corresponding benzyl glycoside (**30**) of **18** was also prepared similarly via **29** from **27**. On the other hand, treatment of 3,4-*O*-dibutylstannylene derivative of **16** with benzyl bromide and tetraethylammonium bromide[10] gave the 4-*O*-benzyl derivative (**33**) predominantly in 70% yield together with **18** in 13% yield. This regioselectivity between two equatorial hydroxyl groups may be noteworthy. Acetohalogeno sugars of D-*xylo* and L-*arabino* configurations were derived from the corresponding acetate (**3**) and nitrate (**8**), respectively. Treatment of **3** with titanium tetrachloride and tetrabromide gave α-chloride (**34**) and α-bromide (**35**) in 77 and 63%, respectively. For the latter, bromination with hydrogen bromide in acetic acid gave a better yield. On the other hand, substitution of **8** with halide ions using tetraethylammonium halides gave β-chloride (**36**) and β-bromide (**37**) in 80 and 55%, respectively. These derivatives should be useful as synthetic intermediates for 2-amino-2-deoxypentose-containing antibiotics such as cinodine.

Experimental

Melting points were determined with a Mel-Temp appara-

tus and are not corrected. Optical rotations were measured using a 0.5-dm tube and a Carl Zeiss LEP-Al or JASCO DIP-4 polarimeter. IR spectra were recorded with a Hitachi EPI-G2 grating spectrometer. ^{1}H NMR spectra were recorded at 100 MHz with a JEOL PS-100 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard, unless stated otherwise. Column chromatography and preparative TLC were performed on Wakogel C-200 (Wako Pure Chemical Industries, Ltd.) and Kieselgel 60 HF_{254} (Merck), respectively. Evaporations were conducted under diminished pressure at 50 °.

Azidonitration of Glycals. To a solution of a glycal acetate (2.0 g, 10 mmol) in acetonitrile (70 ml) was added sodium azide (1.6—4.4 g, 11—30 mmol) and cerium(IV) ammonium nitrate (CAN, 10.9—23.5 g, 20—43 mmol) with stirring and cooling between −10 and −20 °C under nitrogen (occasionally under air). The solution was kept at the same temperature with stirring for 5—6 h, and mixed with ether and water. The ether layer was washed with water, dried and evaporated to give a crude syrupy mixture of 2-azido-1-nitrate derivatives.

1,3,4-Tri-*O*-acetyl-2-azido-2-deoxy-D-xylopyranose (3) and Its α-D-*Lyxo* Isomer (6). A crude mixture of azidonitrates obtained from **1** (17.0 g, 85 mmol), sodium azide (13 g, 200 mmol), and CAN (200 g, 365 mmol) at −20 °C under air as described above, was dissolved in acetic acid (100 ml) and heated at 70 °C for 2 h with stirring in the presence of sodium acetate (10 g). The reaction solution was evaporated and the residue was mixed thoroughly with chloroform and water. The organic layer was separated, dried and evaporated to give a syrup, which was fractionated on a silica-gel column with benzene-acetone (30 : 1) or toluene-ethyl acetate (19 : 1) to give **3** and **6** in 58 and 5% yields, respectively. Compound **3** was proved to be a mixture of α- and β-anomers with an approximate ratio of **10** by ^{1}H NMR.

3: Syrup, IR (NaCl) 2105 (azido) and 1750 (ester) cm^{-1}; ^{1}H NMR α-anomer δ=6.20 (d, $J_{1,2}$=3.9 Hz, H-1), 3.55 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.44 (t, $J_{3,4}$=10.5 Hz, H-3), 4.99 (dt, $J_{4,5}$=10.5 Hz, $J_{4,5'}$=6.0 Hz, H-4), 3.67 (t, $J_{5,5'}$=10.5 Hz, H-5), 3.91 (dd, H-5'), 2.04, 2.12, and 2.18 (each s, OAc), β-anomer δ=5.50 (d, $J_{1,2}$=8.3 Hz, H-1), 3.60 (dd, $J_{2,3}$=9.0 Hz, H-2), 5.10 (t, $J_{3,4}$=9.0 Hz, H-3), 5.0 (H-4), 3.45 (dd, $J_{4,5}$=9.0 Hz, $J_{5,5'}$=11.8 Hz, H-5), 4.10 (dd, $J_{4,5'}$=4.9 Hz, H-5'), 2.04, 2.12, and 2.17 (each s, OAc).

Found: C, 43.89; H, 4.95; N, 13.95%. Calcd for $C_{11}H_{15}N_3O_7$: C, 43.86, H, 5.02; N, 13.95%.

6: Syrup, $[\alpha]_D$ +1.5° (*c* 1.0, $CHCl_3$). ^{1}H NMR δ=5.94 (d, $J_{1,2}$=5.1 Hz, H-1), 3.96 (dd, $J_{2,3}$=3.6 Hz, H-2), 5.36 (dd, $J_{3,4}$=7.1 Hz, H-3), 5.06 (m, H-4), 3.76 (dd, $J_{4,5}$=6.0 Hz, $J_{5,5'}$=12.0 Hz, H-5), 3.98 (dd, $J_{4,5'}$=3.8 Hz, H-5') and 2.06—2.10 (OAc).

Found: C, 43.32; H, 5.07; N, 13.73%. Calcd for $C_{11}H_{15}N_3O_7$: C, 43.86; H, 5.02; N, 13.95%.

Methyl 3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranoside (4) and Its α-D-*Lyxo* Isomer (7). To a solution of the azidonitration reaction (**1** 2.4 g, NaN_3 1.57 g, CAN 26.6 g in CH_3CN 85 ml) carried out for 5.5 h in the same manner as described for **3** was added methanol (80 ml) together with chloroform (40 ml) and anhydrous magnesium sulfate. The mixture was stirred at room temperature for 16 h. Insoluble materials were filtered off and washed with chloroform. The filtrate was washed with water, dried and evaporated to give a syrup, which was fractionated on a silica-gel column with hexane-ethyl acetate (4 : 1) to give **4** in 84% yield and **7** in a trace amount. **4**: Syrup, $[\alpha]_D$ +128.5° (*c* 1.0, $CHCl_3$); IR (NaCl) 2103 (azido) and 1750 (ester) cm^{-1}; ^{1}H NMR δ=4.80 (d, $J_{1,2}$=3.3 Hz, H-1), 3.27 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.46 (dd, $J_{3,4}$=9.6 Hz, H-3), 4.94 (dt, $J_{4,5}$=9.6 Hz, $J_{4,5'}$=6.0 Hz, H-4), 3.80 (dd, $J_{5,5'}$=10.8 Hz, H-5), 3.5 (H-5'), 2.04 and 2.11 (each s, OAc), and 3.46 (s, OMe).

Found: C, 44.39; H, 5.55; N, 15.11%. Calcd for $C_{10}H_{15}N_3O_6$: C, 43.96; H, 5.53; N, 15.38%.

7: Syrup, $[\alpha]_D$ −145.0° (*c* 1.0, $CHCl_3$). ^{1}H NMR δ=4.65 (d, $J_{1,2}$=2.7 Hz, H-1), 3.73 (dd, $J_{2,3}$=3.6 Hz, H-2), 5.10 (dd, $J_{3,4}$=6.3 Hz, H-3), 4.94 (dt, $J_{4,5}$=5.3 Hz, $J_{4,5'}$=3.8 Hz, H-4), 3.41 (dd, $J_{5,5'}$=12.2 Hz, H-5), 4.09 (dd, H-5'), 3.52 (s, OMe), 2.07 and 2.13 (each s, OAc).

Found: C, 43.73; H, 5.35; N, 15.14%. Calcd for $C_{10}H_{15}N_3O_6$: C, 43.96; H, 5.53; N, 15.38%.

Benzyl 3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranoside (5). A crude mixture of azidonitrates obtained from **1** (3.2 g, 16 mmol) in the same manner as described for **3**, was mixed with benzyl alcohol (7.8 ml, 69 mmol) in chloroform (30 ml). The solution was kept at room temperature for 24 h, washed with water, dried and evaporated to give a syrup, which was purified on a silica-gel column with benzene-acetone (30 : 1) to give **5** in 55% yield, $[\alpha]_D$ +104.7° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=4.98 (d, $J_{1,2}$=3.3 Hz, H-1), 3.22 (dd, $J_{2,3}$=10.4 Hz, H-2), 5.49 (dd, $J_{3,4}$=9.2 Hz, H-3), 2.04 and 2.10 (each s, OAc), 4.56 and 4.76 (ABq, J=12.8 Hz, CH_2 in Bn) and 7.36 (s, Ph).

Found: C, 54.83; H, 5.20; N, 11.65%. Calcd for $C_{16}H_{19}N_3O_6$: C, 55.01; H, 5.48; N, 12.03%.

3,4-Di-*O*-acetyl-2-azido-2-deoxy-1-*O*-nitro-β-L-arabinopyranose (8). Azidonitration of **2** (10 mmol) with sodium azide (15 mmol) and CAN (30 mmol) was carried out at −10 °C in the same manner as described for **3**. A crude azido nitrate was purified on silica-gel column to give a syrupy mixture of α- and β-nitrate (55%, α : β = 1.8 : 1) and only the β-anomer (**8**) was obtained as crystal from ether-hexane in 20% yield, mp 107—108.5 °C, $[\alpha]_D$ +18.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=5.57 (d, $J_{1,2}$=8.0 Hz, H-1), 3.86 (dd, $J_{2,3}$=9.7 Hz, H-2), 4.98 (dd, $J_{3,4}$=3.5 Hz, H-3), 5.26 (m, H-4), 4.10 (dd, $J_{4,5}$=2.6 Hz, $J_{5,5'}$=12.6 Hz, H-5), 3.78 (dd, $J_{4,5'}$=1.5 Hz, H-5'), 2.10 and 2.16 (each s, OAc).

Found: C, 35.85; H, 4.04; N, 18.05%. Calcd for $C_9H_{12}N_4O_8$: C, 35.53; H, 3.98; N, 18.42%.

1,3,4-Tri-*O*-acetyl-2-azido-2-deoxy-β-L-arabinopyranose (9). The glycosyl nitrate **8** (1.8 g, 5.6 mmol) was acetolyzed with acetic acid (10 ml) and anhydrous sodium acetate (0.8 g, 9.8 mmol) at 100 °C for 50 min. The residue obtained by direct evaporation of the reaction mixture was dissolved in chloroform. The solution was washed with water, dried and evaporated to give a syrup, which was purified on a silica-gel column with hexane-ethyl acetate (4 : 1) to afford **9** as crystal in 86% yield, mp 97—98 °C, $[\alpha]_D$ +128.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ=6.28 (d, $J_{1,2}$=3.3 Hz, H-1), 3.96 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.31 (dd, $J_{3,4}$=3.0 Hz, H-3), 5.31 (broad s, H-4), 3.80 (dd, $J_{4,5}$=1.8 Hz, $J_{5,5'}$=13.0 Hz, H-5), 4.04 (dd, $J_{4,5'}$=1.4 Hz, H-5'), 2.10 and 2.17 (each s, OAc).

Found: C, 44.12; H, 4.94; N, 13.75%. Calcd for $C_{11}H_{15}N_3O_7$: C, 43.86; H, 5.02; N, 13.95%.

Methyl 3,4-Di-*O*-acetyl-2-azido-2-deoxy-β-L-arabinopyranoside (10). The nitrate **8** (400 mg, 1.3 mmol) was dissolved in absolute methanol (10 ml) and the solution was kept at room temperature overnight with stirring in the

presence of molecular sieve 3 A. After removal of molecular sieve by filtration the filtrate was evaporated and the resulting syrupy residue was purified on preparative TLC on silica gel with benzene-acetone (40:3) to give **10** in 64% yield, $[\alpha]_D$ +218° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.89 (d, $J_{1,2}$= 3.4 Hz, H-1), 3.74 (m, H-2), 5.32 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.0 Hz, H-3), 5.29 (m, H-4), 3.70 (dd, $J_{4,5}$=1.8 Hz, $J_{5,5'}$=13.0 Hz, H-5), 3.96 (dd, $J_{4,5'}$=1.5 Hz, H-5'), 2.10 and 2.18 (each s, OAc), and 3.50 (s, OMe).

Found: C, 44.12; H, 5.27; N, 15.07%. Calcd for $C_{10}H_{15}N_3O_6$: C, 43.96; H, 5.53; N, 15.38%.

Benzyl 3,4-Di-*O*-acetyl-2-azido-2-deoxy-β-L-arabinopyranoside (11). The nitrate **8** (305 mg, 1.09 mmol) was stirred with benzyl alcohol (7 ml) and molecular sieve 3 A overnight at room temperature. The same work-up as described for **10** afforded **11** as a syrup in 90% yield, $[\alpha]_D$ +192° (*c* 1.0, $CHCl_3$); ^1H NMR δ=5.03 (d, $J_{1,2}$=3.3 Hz, H-1), 3.70 (dd, $J_{2,3}$=10.7 Hz, H-2), 5.36 (dd, $J_{3,4}$=3.3 Hz, H-3), 5.33 (broad s, H-4), 3.66 (dd, $J_{4,5}$=1.5 Hz, $J_{5,5'}$=12.5 Hz, H-5), 3.98 (dd, $J_{4,5'}$=1.3 Hz, H-5'), 2.07 and 2.14 (each s, OAc), 4.56 and 4.74 (ABq, J=12.8 Hz, CH_2 in Bn), and 7.34 (s, Ph).

Found: C, 54.82; H, 5.21; N, 12.41%. Calcd for $C_{16}H_{19}N_3O_6$: C, 55.01; H, 5.48; N, 12.03%.

Benzyl 2-*O*-(1-Imidazolylsulfonyl)-3,4-*O*-isopropylidene-β-L-arabinopyranoside (14). To a solution of **12** (1.6 g, 5.7 mmol) in pyridine (6 ml) was added imidazole (2.0 g, 30 mmol) and sulfuryl chloride (1.2 ml, 15 mmol) in two portions with stirring and cooling (ice-water). After being kept overnight at room temperature the mixture was poured into ice-water and extracted twice with chloroform. The extract was washed with water, dried and evaporated to give **14** (1.6 g) as a solid residue, which was characterized only by ^1H NMR δ=4.92 (d, $J_{1,2}$=2.7, H-1), 4.45 (H-2), 4.34 (dd, H-3), 4.20 (bd, H-4), 3.95 (bs, 2 H, H-5 and H-5'), 1.30 and 1.34 (each s, CMe_2), 4.45 and 4.69 (ABq, J=11.6 Hz, CH_2 in Bn), 7.03 (d), 7.87 (d), and 7.23 (dd) (Imidazyl), and 7.31 (s, Ph).

Benzyl 2-Azido-2-deoxy-3,4-*O*-isopropylidene-β-L-ribopyranoside (15). A. From 12 via Its 3-Triflate (13): To a solution of trifluoromethanesulfonic anhydride (1 ml, 7.1 mmol) in dichloromethane (20 ml) was added dropwise at −5—−10 °C a solution of pyridine (1 ml, 12 mmol) in dichloromethane (10 ml) and then a solution of **12** (1 g, 3.6 mmol) in dichloromethane (10 ml). The mixture was kept at the temperature for 0.5 h and then poured into ice-water containing sodium hydrogencarbonate. The dichloromethane layer was separated, washed with dilute hydrochloric acid, water, and sodium chloride solution, dried, and evaporated to give crude **13** as syrup, which was characterized only by ^1H NMR δ=5.09 (d, $J_{1,2}$=3.5 Hz, H-1), 5.37 (dd, $J_{2,3}$=6.9 Hz, H-2), 4.68 (d, H-3), 4.15 (H-4), 4.07 (bs, 2H, H-5 and H-5'), 1.40 and 1.56 (each s, CMe_2), 4.71 and 4.80 (ABq, J=10.0 Hz, CH_2 in Bn), and 7.36 (s, Ph).

A mixture of crude **13** and sodium azide (0.6 g, 9.2 mmol) in *N*,*N*-dimethylformamide (5 ml) was heated at 65—70 °C for 1 h, and then poured into ice-water, dried and evaporated to give a syrupy residue, from which was obtained the compound **15** by column chromatography on silica gel. Syrup, $[\alpha]_D$ +66.8° (*c* 1.1, $CHCl_3$); ^1H NMR δ=4.60 (d, $J_{1,2}$=3.6 Hz, H-1), 4.44 (dd, $J_{2,3}$=8.7 Hz, H-2), 4.7 (H-3), 4.18 (H-4), 4.0 (2 H, H-5 and H-5'), 1.34 and 1.50 (each s, CMe_2), 4.77 (s, CH_2 in Bn), and 7.33 (s, Ph).

Found: C, 58.76; H, 6.14; N, 13.42%. Calcd for $C_{15}H_{19}N_3O_4$: C, 59.01; H, 6.27; N, 13.76%.

B. From 14: A mixture of **14** (410 mg, 1.0 mmol), sodium azide (210 mg, 3.2 mmol), and tetrabutylammonium chloride (340 mg, 3.2 mmol) in toluene (5 ml) was heated under gentle reflux for 6 h. After addition of water the mixture was washed with water three times, dried and evaporated to give **14** (245 mg, 80%), which was identical with the 2-azido sugar described above.

Methyl 2-Azido-2-deoxy-α-D-xylopyranoside (16). Compound **4** (440 mg, 2.3 mmol) was dissolved in methanol containing catalytic amount of sodium. After standing at room temperature for 1 h and neutralization with acetic acid, the solution was evaporated and the residue was purified on a silica-gel column with ethyl acetate and hexane (3:2) to give **16** as a syrup in 82% yield, $[\alpha]_D$ +139.9° (*c* 1.0, methanol).

Found: C, 38.22; H, 5.84; N, 22.70%. Calcd for $C_6H_{11}N_3O_4$: C, 38.09; H, 5.86; N, 22.21%.

Benzoylation of 16. To a solution of **16** (6.11 g, 32.3 mmol) in acetone (70 ml) was added with stirring triethylamine (8.8 ml, 63.2 mmol) and benzoyl chloride (7.6 ml, 65.3 mmol), and the mixture was kept at room temperature for 36 h. After addition of water and further stirring for 2 h, the mixture was extracted with chloroform. The extract was washed with water, dried and evaporated to give a syrupy mixture of benzoates, which was fractionated on a silica-gel column with benzene-acetone (30:1) to give 3,4-dibenzoate (**20**), 4-benzoate (**19**) and 3-benzoate (**17**) in 29, 65, and 5%, respectively.

17: Syrup, $[\alpha]_D$ +134.9° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.82 (d, $J_{1,2}$=3.8 Hz, H-1), 3.40 (dd, $J_{2,3}$=10.5 Hz, H-2), 5.43 (dd, $J_{3,4}$=8.3 Hz, H-3), 3.6—4.1 (m, 3H, H-4, H-5, and H-5'), 3.46 (s, OMe), 7.2—7.6 and 8.0—8.1 (m, Ph).

Found: C, 53.34; H, 5.24; N, 13.96%. Calcd for $C_{13}H_{15}N_3O_5$: C, 53.24; H, 5.16; N, 14.33%.

19: Mp 85—89 °C, $[\alpha]_D$ +46.0° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.75 (d, $J_{1,2}$=3.6 Hz, H-1), 3.32 (dd, $J_{2,3}$=9.3 Hz, H-2), 4.23 (t, $J_{3,4}$=9.3 Hz, H-3), 5.05 (ddd, $J_{4,5}$=10.3 Hz, $J_{4,5'}$= 5.9 Hz, H-4), 3.63, (t, $J_{5,5'}$=10.6 Hz, H-5), 3.89 (dd, H-5'), 3.43 (s, OMe), 7.2—7.6 and 7.9—8.1 (m, Ph).

Found: C, 53.29; H, 5.03; N, 13.85%. Calcd for $C_{13}H_{15}N_3O_5$: C 53.24; H, 5.16; N, 14.33%.

20: Syrup, $[\alpha]_D$ +25.5° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.92 (d, $J_{1,2}$=3.8 Hz, H-1), 3.47 (dd, $J_{2,3}$=9.6 Hz, H-2), 5.95 (t, $J_{3,4}$=9.3 Hz, H-3), 5.31 (ddd, $J_{4,5}$=10.5 Hz, $J_{4,5'}$=6.0 Hz, H-4), 3.78 (t, $J_{5,5'}$=10.5 Hz, H-5), 4.04 (dd, H-5'), 3.52 (s, OMe), 7.3—7.6 and 7.9—8.2 (m, Ph).

Found: C, 59.82; H, 4.73; N, 10.80%. Calcd for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.58%.

Methyl 2-Azido-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (18). Compound **22** was debenzoylated with sodium methoxide in methanol in a conventional manner to give **18** in a quantitative yield, $[\alpha]_D$ +33.8°; ^1H NMR δ=4.66 (d, $J_{1,2}$=3.3 Hz, H-1), 3.2—3.8 (m, H-2—5), 3.47 (s, OMe), 4.68 and 4.88 (ABq, J=10.5 Hz, CH_2 in Bn), and 7.40 (s, Ph).

Found: C, 55.54; H, 6.09; N, 14.89%. Calcd for $C_{13}H_{17}N_3O_4$: C, 55.90; H, 6.14; N, 15.05%.

Methyl 2-Azido-4-*O*-benzoyl-2-deoxy-3-*O*-methylsulfonyl-α-D-xylopyranoside (21). Compound **19** was mesylated with methanesulfonyl chloride in pyridine in a conventional manner to give **21** in 85% yield, mp 53—54 °C, $[\alpha]_D$ −79.1° (*c* 1.0, $CHCl_3$); ^1H NMR δ=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, 3H, H-3, H-4, and H-5), 4.01 (dd, $J_{4,5'}$=5.4 Hz, $J_{5,5'}$=11.3 Hz), 3.47 (s, OMe), 3.04 (s, Ms) and 7.3—7.6 and 8.0—8.15 (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-Azido-4-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (22). To a solution of **19** (527 mg, 1.8 mmol) in dry benzene (5 ml) was added benzyl bromide (0.85 ml, 7.1 mmol) and silver oxide (830 mg, 3.6 mmol) and the mixture was stirred under exclusion of light for 40 h. The undissolved material was filtered off and a residue obtained by evaporation of the filtrate was purified on a silica-gel column with hexane-ethyl acetate (7:1) to give **22** in 74% yield, syrup, $[\alpha]_D$ −52.2° (*c* 1.0, $CHCl_3$); IR (NaCl) 2100 (azido) and 1725 (ester) cm^{-1}; ^1H NMR δ=4.78 (d, $J_{1,2}$=1.2 Hz, H-1), 3.5 (H-2), 4.09 (t, $J_{2,3}=J_{3,4}$=9.5 Hz, H-3), 5.18 (ddd, $J_{4,5}$=10.5 Hz, $J_{4,5'}$=5.9 Hz, H-4), 3.60 (dd, $J_{5,5'}$=11.0 Hz, H-5), 3.90 (dd, H-5'), 3.46 (s, OMe), 4.72 and 4.80 (ABq, *J*= 11.4 Hz, CH_2 in Bn), 7.19 (s, Ph), 7.2—7.6 and 7.9—8.0 (m, Ph).

Found: C, 62.95; H, 5.60; N, 10.69%. Calcd for $C_{20}H_{21}N_3O_5$: C, 62.65; H, 5.52; N, 10.96%.

Methyl 2-Azido-4-*O*-benzoyl-2-deoxy-α-D-ribopyranoside (24). To a solution of **19** (1.7 g, 5.8 mmol) and dimethyl sulfoxide (2.3 g, 29.5 mmol) in dry dichloromethane (10 ml) was added with stirring at −78 °C a solution of trifluoroacetic anhydride (3.5 g, 1.8 mmol) in dry dichloromethane (5 ml), and then after 30 min, a solution of triethylamine (4.3 g, 43 mmol) in dichloromethane (5 ml). The temperature was kept for further 30 min and raised up to room temperature. Then, to the reaction solution was added with stirring methanol (20 ml) and sodium borohydride (0.43 g, 12 mmol) and the stirring was continued for 30 min. After addition of chloroform the reaction solution was washed with water, dried and evaporated to give a syrupy residue, which was purified on a silica-gel column with hexane-ethyl acetate (5:1) to afford **24** in 75% yield, $[\alpha]_D$ +110.3° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.78 (d, $J_{1,2}$=3.0 Hz, H-1), 3.43 (t, $J_{2,3}$=3.0 Hz, H-2), 4.43 (dt, $J_{3,4}$=3.0 Hz, $J_{3,OH}$=9.6 Hz, H-3), 5.07 (ddd, $J_{4,5}$=9.8 Hz, $J_{4,5'}$=5.1 Hz, H-4), 4.04 (dd, $J_{5,5'}$=11.4 Hz, H-5), 3.76 (dd, H-5'), 3.36 (d, OH), 3.56 (s, OMe), 7.3—7.6 and 8.0—8.2 (m, Ph).

Found: C, 53.83; H, 5.15; N, 14.03%. Calcd for $C_{13}H_{15}N_3O_5$: C, 53.24; H, 5.16; N, 14.33%.

Methyl 3-*O*-Acetyl-2-azido-4-*O*-benzoyl-2-deoxy-α-D-ribopyranoside (25). Acetylation of **24** in a usual manner gave **25** in 88% yield, syrup, $[\alpha]_D$ +60.2° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.66 (d, $J_{1,2}$=3.0 Hz, H-1), 3.5 (H-2), 5.54 (t, $J_{2,3}$=3.3 Hz, H-3), 5.21 (dt, $J_{3,4}$=3.3 Hz, H-4), 4.12 (dd, $J_{4,5}$=7.4 Hz, $J_{5,5'}$=11.6 Hz, H-5), 3.70 (dd, $J_{4,5'}$=3.9 Hz, H-5'), 2.13 (s, OAc), 3.55 (s, OMe), 7.3—7.6 and 7.9—8.1 (m, Ph).

Found: C, 53.41; H, 5.03; N, 12.20%. Calcd for $C_{15}H_{17}N_3O_6$: C, 53.73; H, 5.11; N, 12.53%.

Benzyl 2-Azido-2-deoxy-α-D-xylopyranoside (26). Compound **5** was deacetylated in the same manner as described for **16** and crude **26** was purified on a silica-gel column with hexane-ethyl acetate (2:1). Syrup, $[\alpha]_D$ +88.7° (*c* 1.0, methanol); ^1H NMR δ=4.91 (d, $J_{1,2}$=3.5 Hz, H-1), 3.15 (dd, $J_{2,3}$=9.5 Hz, H-2), 3.40—4.10 (m, other ring protons), 4.52 and 4.75 (ABq, *J*=12.0 Hz, CH_2 in Bn), and 7.35 (s, Ph).

Found: C, 54.10; H, 5.64; N, 15.81%. Calcd for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; N, 15.84%.

Benzyl 2-Azido-4-*O*-benzoyl-2-deoxy-α-D-xylopyranoside (27) and Benzyl 2-Azido-3,4-di-*O*-benzoyl-2-deoxy-α-D-xylopyranoside (28). To a solution of **26** (2.42 g, 9.1 mmol) in acetone (30 ml) was added under cooling with ice-water triethylamine (2.5 ml, 18 mmol) and benzoyl chloride (1.6 ml, 14 mmol), and the mixture was stirred at room temperature for 16 h. A syrupy mixture of benzoates obtained by usual work-up was fractionated on a silica-gel column with benzene-acetone (100:1) to give 3,4-dibenzoate (**28**) and 4-benzoate (**27**) in 15 and 66% yields, respectively.

27: Mp 94—95 °C, $[\alpha]_D$ +64.5° (*c* 1.2, $CHCl_3$); ^1H NMR δ=5.04 (d, $J_{1,2}$=3.6 Hz, H-1), 3.37 (dd, $J_{2,3}$=10.5 Hz, H-2), 4.37 (t, $J_{3,4}$=9.3 Hz, H-3), 5.16 (m, H-4), 3.77 (t, $J_{4,5}=J_{5,5'}$=10.5 Hz, H-5), 3.99 (dd, $J_{4,5'}$=6.3 Hz, H-5'), 4.63 and 4.94 (ABq, *J*=11.4 Hz, CH_2 in Bn), 7.46 (s, Ph), 7.4—7.7 and 8.0—8.2 (m, Ph).

Found: C, 62.46; H, 5.18; N, 11.25%. Calcd for $C_{19}H_{19}N_3O_5$: C, 61.78; H, 5.19; N, 11.38%.

28: Syrup, $[\alpha]_D$ +37.9° (*c* 1.3, $CHCl_3$); ^1H NMR δ=5.17 (d, $J_{1,2}$=3.3 Hz, H-1), 3.49 (dd, $J_{2,3}$=10.2 Hz, H-2), 6.08 (dd, $J_{3,4}$=9.9 Hz, H-3), 5.40 (dt, $J_{4,5}$=9.9 Hz, $J_{4,5'}$=6.0 Hz, H-4), 3.90 (t, H-5), 4.14 (dd, $J_{5,5'}$=11.0 Hz, H-5'), 4.68 and 4.90 (ABq, *J*=11.6 Hz, CH_2 in Bn), 7.46 (s, Ph), 7.3—7.7 and 8.0—8.3 (m, Ph).

Found: C, 65.73; H, 4.87; N, 8.95%. Calcd for $C_{26}H_{23}N_3O_6$: C, 65.95; H, 4.90; N, 8.88%.

Benzyl 2-Azido-4-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (29). Compound **27** was benzylated in the same manner as described for **22** and the product was purified on a silica-gel column with hexane-ethyl acetate (1:0—4:1) to give **29** in 86% yield, syrup, $[\alpha]_D$ −6.2° (*c* 1.1, $CHCl_3$); ^1H NMR δ=5.04 (d, $J_{1,2}$=3.6 Hz, H-1), 3.50 (dd, $J_{2,3}$=10.1 Hz, H-2), 4.24 (t, H-3), 5.29 (ddd, $J_{3,4}$=9.6 Hz, $J_{4,5}$=10.2 Hz, $J_{4,5'}$=6.0 Hz, H-4), 3.74 (t, H-5), 4.01 (dd, $J_{5,5'}$=10.7 Hz, H-5'), 4.64 and 4.84 (ABq, *J*=12.0 Hz, CH_2 in Bn), 4.82 and 4.88 (ABq, *J*=11.3 Hz, CH_2 in Bn), 7.30 and 7.45 (each s, Ph), 7.3—7.7 and 8.0—8.3 (m, Ph).

Found: C, 67.92; H, 5.50; N, 8.86%. Calcd for $C_{26}H_{25}N_3O_5$: C, 67.96; H, 5.48; N, 9.15%.

Benzyl 2-Azido-3-*O*-benzyl-2-deoxy-α-D-xylopyranoside (30). Compound **29** was debenzoylated in the same manner as described for **18** to give **30** in a quantitative yield, mp 88—91 °C, $[\alpha]_D$ +50.9° (*c* 0.9, $CHCl_3$); ^1H NMR δ=4.97 (d, $J_{1,2}$=3.0 Hz, H-1), 3.33 (dd, $J_{2,3}$=9.0 Hz, H-2), 3.6—4.0 (m, 4H, H-3, H-4, H-5, and H-5'), 4.61 and 4.83 (ABq, *J*=12.0 Hz, CH_2 in Bn), 4.79 and 4.97 (ABq, *J*=11.3 Hz, CH_2 in Bn), and 7.44 (bs, Ph).

Found: C, 64.52; H, 5.94; N, 11.41%. Calcd for $C_{19}H_{21}N_3O_4$: C, 64.21; H, 5.96, N, 11.82%.

Methyl 3,4-Anhydro-2-azido-2-deoxy-α-D-ribopyranoside (31). Compound **21** (6.74 g, 18.1 mmol) was dissolved in 1.4 M (1M=1 mol dm^{-3}) methanolic potassium hydroxide (140 ml) and the solution was refluxed for 5 min. After addition of water the reaction mixture was extracted with chloroform. The extract was washed with water, dried and evaporated to give a syrupy residue, which was purified on a silica-gel column with benzene-ethanol (80:1). Yield 76%, mp 64—65 °C, $[\alpha]_D$ −16.8° (*c* 1.0, $CHCl_3$); ^1H NMR δ=4.60 (d, $J_{1,2}$=4.2 Hz, H-1), 3.2—3.6 (m, 3H, H-2, H-3, and H-4), 4.15 (bd, $J_{4,5}$=0.5 Hz, $J_{5,5'}$=13.7 Hz, H-5), 4.91 (dd, $J_{4,5'}$=3.0 Hz, H-5') and 3.50 (s, OMe).

Found: C, 44.05; H, 5.84; N, 20.49%. Calcd for $C_{10}H_{16}N_4O_5$: C, 44.11; H, 5.92; N, 20.58%.

Methyl 3,4-Di-*O*-acetyl-2-azido-2-deoxy-β-L-lyxopyranoside (32). To a solution of **31** (222 mg, 1.30 mmol) in dry *N*,*N*-dimethylformamide (10 ml) was added acetic acid (1 ml) and anhydrous sodium acetate (1 g), and the mixture was

heated with stirring at 100 °C for 16 h. After addition of acetic anhydride (3 ml) and pyridine (5 ml) the mixture was heated further at 100 °C for 1 h and then kept at room temperature for 4 h. The mixture was poured into ice-water and extracted five times with toluene. The extract was washed successively with water, 1 M hydrochloric acid, saturated sodium hydrogencarbonate, and water, and dried and evaporated to give a syrupy mixture. The mixture was fractionated on a silica-gel column with hexane-ethyl acetate (4 : 1) to give **32** (193 mg, 54%) and **4** (87 mg, 25%). **32**: Mp 79 °C (from ether), $[\alpha]_D$ +146.5° (*c* 1.8, $CHCl_3$), ^1H NMR δ=4.69 (d, $J_{1,2}$=3.0 Hz, H-1), 3.77 (t, $J_{2,3}$=3.5 Hz, H-2), 5.14 (dd, $J_{3,4}$=6.5 Hz, H-3), 4.97 (ddd, $J_{4,5}$=5.5 Hz, $J_{4,5'}$=3.5 Hz, H-4), 3.43 (dd, $J_{5,5'}$=12.5 Hz, H-5), 4.12 (dd, H-5'), 2.06 and 2.12 (each s, OAc), and 3.51 (s, OMe).

Found: C, 43.30; H, 5.48; N, 14.93%. Calcd for $C_{10}H_{15}N_3O_6$: C, 43.96; H, 5.53; N, 15.38%.

Methyl 2-Azido-4-*O*-benzyl-2-deoxy-α-D-xylopyranoside (33). A mixture of **16** (7.1 g, 38 mmol) and dibutyltin oxide (9.5 g, 38 mmol) in dry benzene (300 ml) was heated under reflux for 1 h. To this mixture was added benzyl bromide (9.1 ml, 77 mmol) and tetraethylammonium bromide (12.9 g, 61 mmol). Being heated under reflux for 17 h, the mixture was evaporated and the residue was fractionated on a silica-gel column with hexane-ethyl acetate (5 : 1) to give **33** and **18** in 70 and 13% yields, respectively. **33**: Syrup, $[\alpha]_D$ +94.5° (*c* 0.9, $CHCl_3$); IR (NaCl) 3450 (OH), and 2110 (azido) cm^{-1}. ^1H NMR δ=4.68 (d, $J_{1,2}$=3.9 Hz, H-1), 3.18 (dd, $J_{2,3}$=10.4 Hz, H-2), 3.38 (s, OMe), 4.64 (s, CH_2Ph), and 7.32 (s, Ph).

Found: C, 55.91; H, 5.81; N, 14.65%. Calcd for $C_{13}H_{17}N_3O_4$: C, 55.90; H, 6.14; N, 15.05%.

3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranosyl Chloride (34). To a solution of **3** (810 mg, 2.69 mmol) in dry dichloromethane (20 ml) was added titanium tetrachloride (1.0 g, 5.3 mmol). The solution was kept overnight at 25—30 °C diluted with chloroform, washed successively with ice-water, saturated aqueous sodium hydrogencarbonate, water, dried and evaporated to give crude **34** (660 mg, 88%), which was purified on a silica-gel column with hexane-ethyl acetate (4 : 1). Yield, 77%, mp 71—72 °C, $[\alpha]_D$ +149.4° (*c* 1.0, $CHCl_3$); ^1H NMR δ=6.10 (d, $J_{1,2}$=3.3 Hz, H-1), 3.78 (dd, $J_{2,3}$=9.8 Hz, H-2), 5.54 (t, $J_{3,4}$=9.8 Hz, H-3), 5.03 (dt, $J_{4,5}$=9.8 Hz, $J_{4,5'}$=6.9 Hz, H-4), 3.9—4.1 (m, H-5,5'), 2.07 and 2.10 (each s, OAc).

Found: C, 39.40; H, 4.37; N, 15.07%. Calcd for $C_9H_{12}N_3O_5Cl$: C, 38.93; H, 4.36; N, 15.13%.

3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-D-xylopyranosyl Bromide (35). (a) With Titanium Tetrabromide: To a solution of **3** (430 mg, 1.43 mmol) in a mixture of dichloromethane (30 ml) and ethyl acetate (3 ml) was added titanium tetrabromide (2.10 g, 5.71 mmol). The mixture was kept at 25—30 °C for 36 h, poured into ice-water, and extracted with chloroform. A similar work-up of the extract as described for **34** gave a crude crystal (440 mg, 63%), mp 95—97 °C (dry ether), $[\alpha]_D$ +189.0° (*c* 1.5, $CHCl_3$); ^1H NMR δ=6.34 (d, $J_{1,2}$=4.0 Hz, H-1), 3.69 (dd, $J_{2,3}$=9.8 Hz, H-2), 5.47 (t, $J_{3,4}$=9.8 Hz, H-3), 5.00 (m, H-4), 3.88 (t, $J_{4,5}$=$J_{5,5'}$=10.5 Hz, H-5), 4.02 (dd, $J_{4,5'}$=6.3 Hz, H-5'), 2.06 and 2.12 (each s, OAc).

Found: C, 33.33; H, 3.63; N, 12.78%. Calcd for $C_9H_{12}N_3O_5Br$: C, 33.56; H, 3.76; N, 13.05%.

(b) With Hydrogen Bromide. To a solution of **3** (500 mg, 1.66 mmol) in dichloromethane (2 ml) was added dropwise a solution of 30% hydrogen bromide in acetic acid (0.6 ml) at 0 °C with stirring. The mixture was kept at the same temperature for 3 h and worked up in the same manner as described above to give **35** in 88% yield.

3,4-Di-*O*-acetyl-2-azido-2-deoxy-β-L-arabinopyranosyl Chloride (36). To a solution of **8** (3.5 g, 11 mmol) in acetonitrile (10 ml) was added tetraethylammonium chloride (7.0 g, 42 mmol). The mixture was stirred at room temperature for 16 h, diluted with chloroform, washed with water, dried and evaporated to give crude **36**, which was purified with hexane-ethyl acetate (4 : 1). Yield, 80%, mp 80—82 °C, $[\alpha]_D$ +185.7° (*c* 1.0, $CHCl_3$); ^1H NMR δ=6.16 (d, $J_{1,2}$=3.3 Hz, H-1), 4.12 (m, H-2), 5.34 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3.0 Hz, H-3), 5.39 (dt, H-4), 3.89 (dd, $J_{4,5}$=1.8 Hz, $J_{5,5'}$=13.8 Hz, H-5), 4.26 (dd, $J_{4,5'}$=1.4 Hz, H-5'), 2.09 and 2.16 (each s, OAc).

Found: C, 38.65; H, 4.52; N, 14.86%. Calcd for $C_9H_{12}N_3O_5Cl$: C, 38.93; H, 4.36; N, 15.13%.

3,4-Di-*O*-acetyl-2-azido-2-deoxy-β-L-arabinopyranosyl Bromide (37). To a solution of **8** (1.0 g, 3.1 mmol) in acetonitrile (10 ml) was added lithium bromide (1.2 g, 14 mmol) and the mixture was kept at room temperature for 3 h. The same work-up as described for **36** gave **37** in 55% yield. ^1H NMR δ=6.47 (d, $J_{1,2}$=4.0 Hz, H-1), 4.03 (H-2), 5.32 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=3.6 Hz, H-3), 5.37 (broad s, H-4), 3.92 (dd, $J_{4,5}$=1.5 Hz, $J_{5,5'}$=13.8 Hz, H-5), 4.22 (dd, $J_{4,5'}$=0.9 Hz, H-5'), 2.07 and 2.15 (each s, OAc).

Found: C, 33.58; H, 3.91; N, 12.73%. Calcd for $C_9H_{12}N_3O_5Br$: C, 33.56; H, 3.76; N, 13.00%.

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