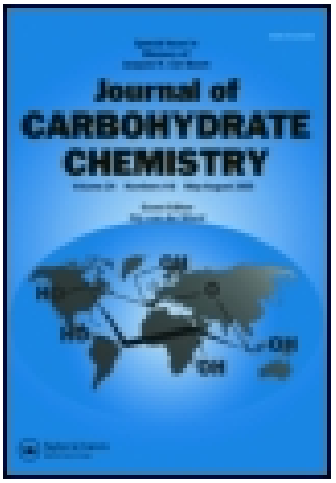

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SYNTHESIS AND REACTIONS OF 3-*C*-BRANCHED-CHAIN ANALOGUES OF 3,6-ANHYDRODEOXYNOJIRIMYCIN[1]

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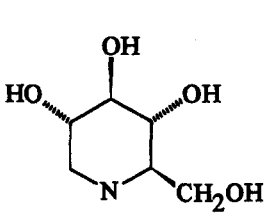
ABSTRACT

The syntheses of 3,6-anhydro-1-deoxy-3-*C*-ethoxycarbonylmethyl- (**4**) and 3-*C*-(2-hydroxyethyl)nojirimycin (**5**) from 5-azido-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**8**) are described. The key intermediate is 5-azido-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethylene-1,2-*O*-isopropylidene-α-D-*ribo*-hex-3-enofuranose (**11**) which was obtained by condensation of 5-azido-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulofuranose (**10**) with (ethoxycarbonylmethylene)triphenylphosphorane. Conventional benzoylation of **4** resulted in the formation of the lactones **13a** and **13b**. The 3-*C*-(2-hydroxyethyl) analogue (**5**) was synthesized by lithium aluminum hydride reduction of 3,6-anhydro-5-azido-5-deoxy-3-*C*-ethoxycarbonylmethyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**12**), followed by deacetalation, and hydrogenation.

INTRODUCTION

Mono- and bicyclic polyhydroxylated alkaloids such as deoxynojirimycin (**1**), castanospermine (**2**) and swainsonine (**3**) are potent glycosidase inhibitors[4] which inhibit enzymes involved with glycogenolysis,[5] glycoprotein processing[6] and saccharides hydrolysis.[7] These compounds exert their biological activity by mimicking the enzymes' normal carbohydrate

substrate. The chemotherapeutic potentials of these compounds have made them the subject of considerable recent research. Since *C*-branched-chain sugars are commonly found as the glycosidic components of substances having physiological activity, such as antibiotics[8] and nucleotides,[9] we became interested in facile syntheses of *C*-branched-chain derivatives of these alkaloids. We now describe the synthesis and reactions of 3,6-anhydro-1-deoxy-3-*C*-ethoxycarbonylmethyl- (**4**) and 3,6-anhydro-1-deoxy-3-*C*-(2-hydroxyethyl)nojirimycin (**5**).



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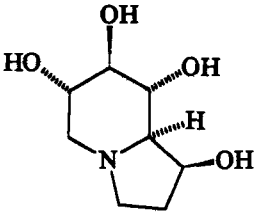

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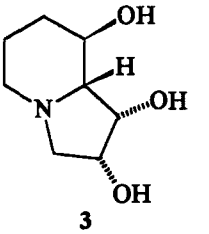

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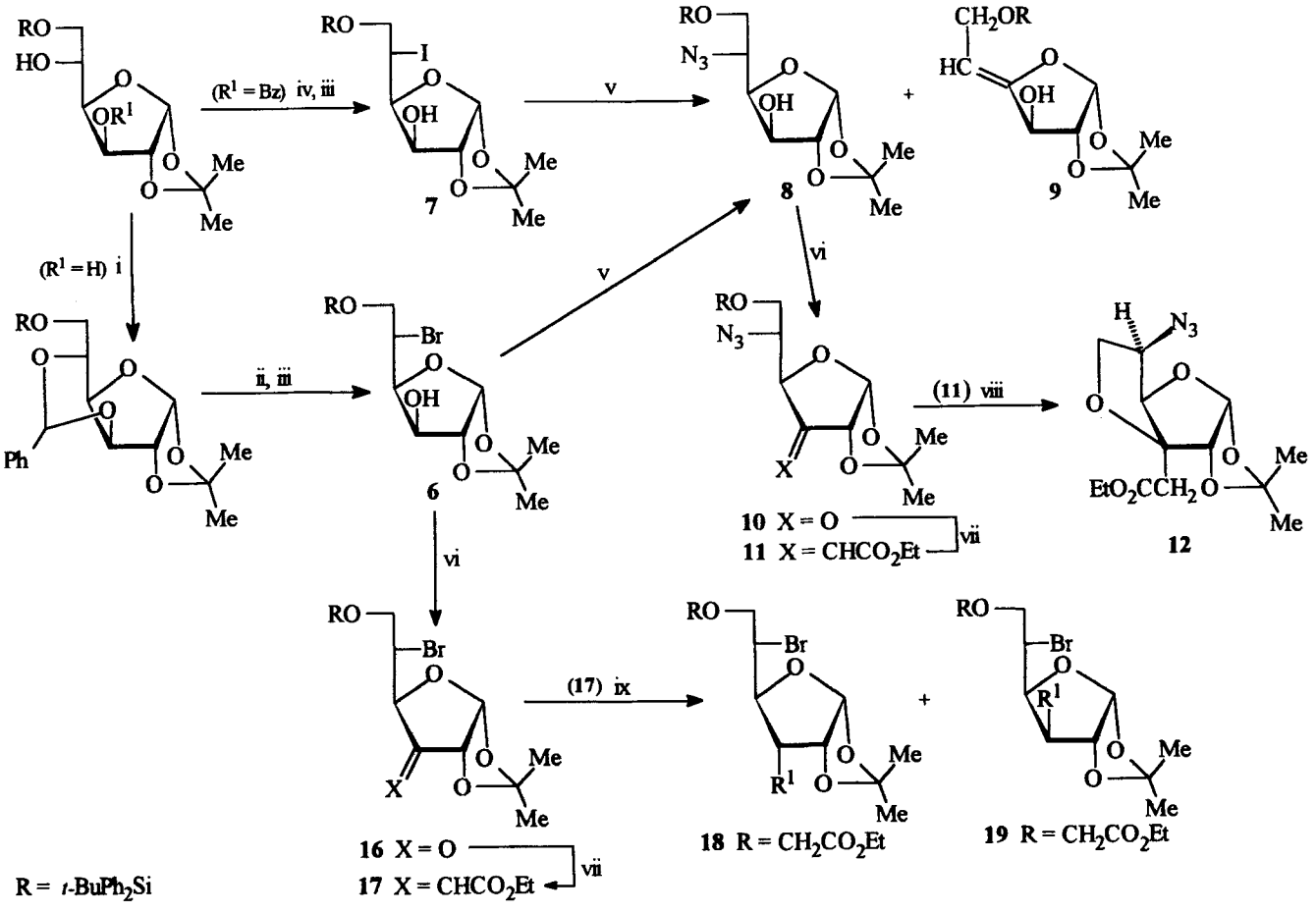
RESULTS AND DISCUSSION

We chose as our starting materials, 5-bromo-[10] (**6**) and 5-iodo-5-deoxy-6-*O*-*tert*-butyldiphenylsilyl-β-L-idofuranose (**7**) (Scheme 1). The 3-*O*-benzoyl derivative of **6** was obtained from 3,5-*O*-benzylidene-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucofuranose[10] by reaction with *N*-bromosuccinimide,[11] while that of **7** was obtained from 3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-glucofuranose by treatment with triphenylphosphine-iodine-imidazole.[12] Deacylation[13] and then azide displacement of the halogen substituent of these derivatives gave 5-azido-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-α-D-glucofuranose (**8**) together with 6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-*threo*-4-enofuranose (**9**) (ratio of **8**:**9** was 3:1 from **6**, and 7:4 from **7**).

The introduction of a *C*-3 alkyl-chain into **8** was readily achieved by condensation of 5-azido-6-*O*-*tert*-butyldiphenyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulofuranose (**10**) with (ethoxycarbonylmethylene)triphenylphosphorane.[14] The reaction produced a 6:1 mixture of (*Z*,*E*)-3-*C*-ethoxycarbonylmethylene derivatives (**11a** and **11b**) in over 78% yield. The major product was shown by NOE difference spectroscopy to be the *Z*-isomer since irradiation of H-3' in **11a** showed a strong enhancement of H-4 but not of H-2; irradiation of H-2 showed only enhancement of H-1.

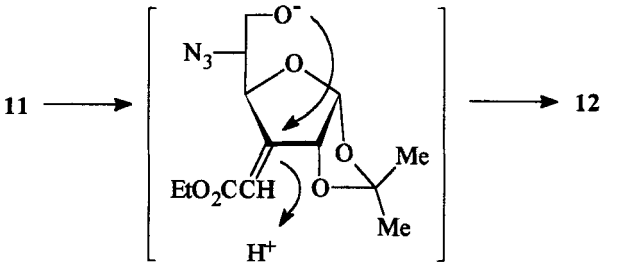
Treatment of **11** with tetra-*n*-butylammonium fluoride in dry tetrahydrofuran gave 3,6-anhydro-5-azido-3-*C*-ethoxycarbonylmethyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**12**). The reaction did not produce the C-6 hydroxyl derivative. This Michael-type addition reaction has



Reagents and conditions: i. PhCHO, $ZnCl_2$, rt, 6 h; ii. NBS, CCl_4, $BaCO_3$, reflux, 2.5 h; iii. M NaOMe, MeOH, rt, 2.5 h; iv. PhP_3-I_2-imidazole, 80 °C, 2.5 h; v. NaN_3, DMF, 90 °C, 5 h; vi. PDC-AcOH, rt, 4.5 h; vii. $PhP_3{=}CHCO_2Et$, CHCl, rt, 7 h; viii. n-$Bu_4N^+F^-$, rt, 5 h; ix. Pd, H_2, rt, 6 h.

Scheme 1

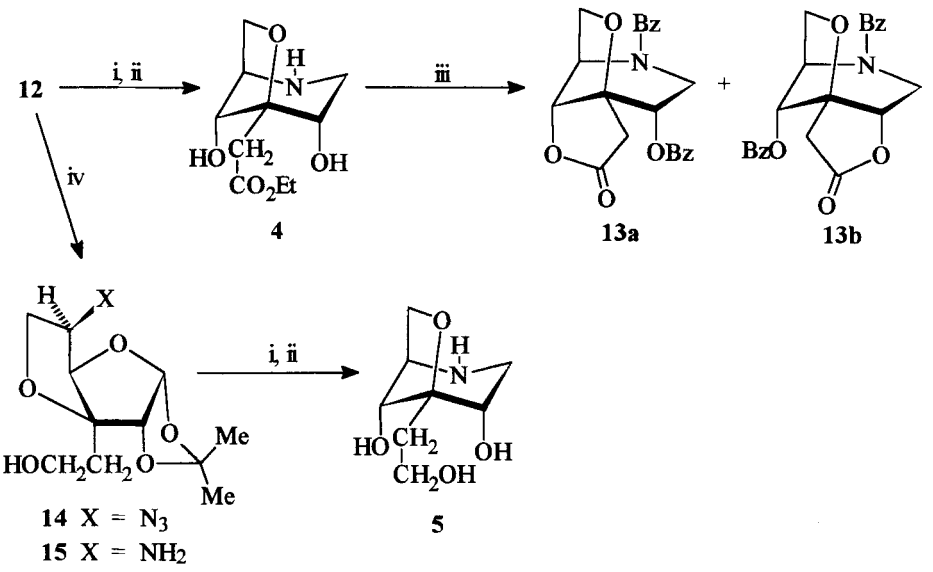
similarly been observed[15] when an α,β-unsaturated ester is in close proximity to a hydroxyl group (6-OH) leading to formation of a 5-membered anhydro ring (**12**).



The structure of **12** was consistent with its ^{1}H and ^{13}C NMR data, the assignments being from an HMQC spectrum. The ^{1}H NMR spectrum of **12** did not show the presence of a lowfield olefinic proton. Instead, two doublets, due to H-3a',3b', were observed at δ 2.68 and 2.91 ($J_{3a',3b'}$ 15.8 Hz). Its ^{13}C NMR spectrum also showed that C-3 (δ 91.5) and C-6 (δ 68.7) resonate downfield (by ~16 and 3 ppm) when compared with those of 5-bromo-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethyl-1,2-*O*-isopropylidene-β-L-talofuranose (**18**) and other 5-azido-1,2-*O*-isopropylidene-α-D-glucofuranose derivatives,[10] indicating involvement of C-3 and C-6 in the formation of the 3,6-anhydro ring. Accurate mass measurement showed a fragment at *m/z* 298, corresponding to $C_{12}H_{16}N_3O_6$ [M^+-15], which is typical of isopropylidene acetals.

Deacetalation of **12** by treatment with Amberlite 120 (H^+) resin, and then hydrogenation over palladium hydroxide-on-charcoal catalyst gave 3,6-anhydro-1-deoxy 3-*C*-ethoxycarbonylmethylnojirimycin (**4**) (Scheme 2). The ^{1}H NMR spectrum of **4** showed the presence of a deoxy group at C-1 (δ 3.48, $J_{1a,2}$ 4.2 Hz, H-1a, and δ 3.21, d, $J_{1a,1b}$ 14.8 Hz, H-1b). Examination of molecular models revealed that the slight deformation of the pyranosyl ring, in order to accommodate the anhydro bridge, caused the H-1b–H-2 (and also H-5–H-6b) dihedral angle to be ~90° and hence a zero coupling would be predicted. The small $J_{4,5}$ coupling (2.8 Hz) is also consistent with the $^{1}C_4$ conformation of the fused-bridge system.[16]

Attempts to characterise compound **4** further by benzoylation resulted in the formation of a (2:1) mixture of isomeric lactones **13a** and **13b**. All attempts to separate the mixture failed. The ^{1}H and ^{13}C NMR spectra of **13a,b** showed the absence of an ethoxy substituent and only two benzoyl groups were evident. The ^{1}H NMR chemical shifts of the lactones were assigned from their NOE and HMBC spectra. The signals due to H-2 and H-4 in both isomers were observed downfield by >1 and >0.8 ppm, respectively, compared to those of **4**,



Reagents and conditions: i. Amberlite IR 120 (H^+), 40 °C; 31 h; ii. $Pd(OH)_2$, H_2, ~6 h; iii. BzCl, pyr, rt, 5 h; iv. LAH, THF, rt, 3 h.

Scheme 2

indicating that these protons were deshielded. Examination of molecular models showed that the formation of the lactones (**13a,b**) tended to deform the $^1C_4$ pyranose ring towards the boat $B_{1,4}$ conformation. The flattening of the ring at C-1 caused the two hydrogen atoms at C-1 to become pseudo-axial and pseduo-equatorial; thus, the large observed $J_{1a,2}$ and $J_{1b,2}$ couplings (7.1-8.9 Hz) for both the isomers.

An attempt to reduce the lactones gave a product which did not appear to be 3,6-anhydro-1-deoxy-3-*C*-(2-hydroxyethyl)nojirimycin (**5**) but we were unable to characterise the compound. We, therefore, carried out the synthesis of **5** by first reducing the ester function in **12** using lithium aluminium hydride [which produced a 14:3 mixture of 3,6-anhydro-5-amino- (**14**) and 5-azido-5-deoxy-3-*C*-hydroxyethyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**15**)], and then deacetalation and catalytic hydrogenation (Scheme 2). The structure of **5** was consistent with its ^1H and ^{13}C NMR data.

We have also synthesised **11** from 5-bromo-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethylene-1,2-*O*-isopropylidene-β-L-*lyxo*-hex-3-enofuranose (**16**) by azide displacement reaction (Scheme 1). Only the *Z*-isomer of **17** was formed when **16** was reacted with (ethoxycarbonylmethylene)triphenylphosphorane. On hydrogenation (Pd/H_2), **17** gave a 3:2

mixture of L-*talo* (**18**) and L-*ido* epimers (**19**). The ^{1}H NMR spectra of **18** and **19** were not well resolved but the large $J_{4,5}$ value (7.2 Hz) for **19** is consistent with the L-*ido* configuration.[10,17]

The lactones **13a,b**, and the 3-*C*-(2-hydroxyethyl) analogue (**5**) were tested against a wide range of enzymes originating from intestinal homogenates from mouse, guinea pig, *Zophobas morio* and *Myzus persicae* larvae, and *Saccharomyces cerivesiae* β-glucosidase, *Penicillum* β-fructofuranosidase and *Aspergillus niger* amyloglucosidase by methods described elsewhere.[18] The compounds showed virtually no inbitory activity against all these enzymes. This is most probably because the piperidine ring has the $^1C_4$ chair conformation.

EXPERIMENTAL

General methods. Optical rotations were determined at 22-25 °C in a 1 dm tube with a Perkin Elmer 141 polarimeter. The ^{1}H and ^{13}C NMR spectra (internal Me_4Si) were recorded on a Brucker AMX-500 (500 MHz) spectrometer. EI mass spectra (70 eV) were determined with a Micromass VG 7-35 spectrometer. Melting points were determined using a Büchi 512 melting point apparatus and are uncorrected. Microanalyses were carried out using a Perkin Elmer 2400 elemental Analyser. Reactions were monitored by TLC on glass plates coated with silica gel 60 F_{254} (Merck); detection was effected by observation under short wavelength UV light (254 nm), then spraying them with 10% sulphuric acid in ethanol and charring them on a hot plate. 1-Deoxynojirimycin derivatives were visualised using ninhydrin solution. Flash-column chromatography was performed on Kieselgel 60 (Merck 230-400 mesh) at 5-10 psi.

6-*O*-*tert*-Butyldiphenylsilyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-β-L-idofuranose (7). A mixture of 3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-glucofuranose (56 g), triphenylphosphine (26.5 g, 1 equiv) and imidazole (13.6 g, 2 equiv) in xylene (450 mL) was heated to 80 °C with stirring under nitrogen, and iodine (27.9 g, 1.1 equiv) was added slowly over 2.5 h. The mixture was stirred at 140 °C for 24 h when TLC (hexane-EtOAc, 4:1) indicated the formation of a major and traces of two minor fast-moving compounds. The hot mixture was poured into satd aq $NaHSO_3$ and stirred for about 10 min. The organic phase was dried ($NaSO_4$), filtered, and concentrated. Flash-column chromatography (hexane-EtOAc, 10:1) of syrupy residue gave 3-*O*-benzoyl 6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-β-L-idofuranose (48.9 g, 72.8%), $[\alpha]_D$ +4.7° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.2-7.9 (m, 10H, 2 Ph); 5.92 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1); 5.34 (d, 1H, $J_{3,4}$ = 2.9 Hz, H-3); 4.66 (dd, 1H, $J_{4,5}$ = 8.8 Hz, H-4); 4.67 (d, 1H, H-2);

4.31 (ddd, 1H, $J_{5,6a}$ = 4.2 Hz, $J_{5,6b}$ = 4.6 Hz, H-5); 3.79 (dd, 1H, $J_{6a,6b}$ = 11.6 Hz, H-6a); 3.71 (dd, 1H, H-6b); 1.49, 1.25 [2s, 2x3H, $C(CH_3)_2$]; 0.99 (s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 111.3 (s, CMe_2); 102.7 (s, C-1); 83.2 (s, C-2); 79.2 (s, C-4); 74.9 (s, C-3); 65.7 (s, C-6); 27.6 (s, C-5); 25.7, 25.6, 25.3 [3s, $C(CH_3)_2$]; 25.7 [s, $C(CH_3)_3$] 18.3 [s, $C(CH_3)_3$]. *m/z*: 657 (M^+-15, 1.2%); 557 (5.0%); 434 (1.8%); 308 (5.6%); 199 (57.7%); 105 (100%).

Anal. Calcd for $C_{32}H_{37}IO_6Si$ (672.63): C, 57.14; H, 5.54; I, 18.87. Found: C, 57.37; H, 5.75; I, 18.59.

A methanolic solution of the 3-*O*-benzoate (40 g in 350 mL) was treated with methanolic 0.5 M sodium methoxide (45 mL) for 4 h at room temperature, then deionised with Duolite MB 5113 mixed-bed resin, filtered, and concentrated, to give **7** (26.5 g, 78.3%), $[\alpha]_D$ +1.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.7-8.4 (m, 10H 2 Ph); 5.95 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1); 4.68 (d, 1H, H-2); 4.3-4.4 (m, 3H, H-3,6a,6b); 4.03 (dd, 1H, $J_{3,4}$ = 2.2 Hz, $J_{4,5}$ = 11.9 Hz, H-4); 3.8-3.9 (m, 1H, H-5); 3.30 (d, 1H, $J_{3\text{-OH}}$ 3.3 Hz, OH-3); 1.52, 1.33 [2s, 2 x 3H, $C(CH_3)_2$]; 1.08 (s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 111.75 (s, CMe_2); 103.9 (s, C-1); 85.7 (s, C-2); 85.5 (s, C-4); 74.9 (s, C-3); 67.2 (s, C-6); 26.9, [2s, $C(CH_3)_2$]; 26.8 [s, $C(CH_3)_3$]; (26,3 (s, C-5); 19.1 [s, $C(CH_3)_3$]. *m/z*: 553 (M^+-15, 2.35%); 480 (3.9%); 474 (3.1%); 236 (3.1%); 207 (6.2%); 199 (100%); 42 (81.3%).

Anal. Calcd for $C_{25}H_{33}IO_5Si$ (568.52): *C*, 52.82; *H*, 5.85; *I*, 22.32. Found: C, 52.57; H, 6.14; I, 22.66.

5-Azido-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexos-3-ulofuranose (10). A solution of **6**[10] or **7** (4.3 g) in *N,N*-dimethylformamide (50 mL) was stirred with sodium azide (4.4g) for at 90 °C for ~5 h under argon. TLC (hexane-EtOAc, 5:2) then showed two faster moving compounds with very similar R_F values. The mixture was poured into ice-water and extracted with ethyl acetate, the extract was dried ($NaSO_4$) and concentrated to give syrupy **8** and **9** (**6** → 62.3%, 3:1 ratio of **8**:**9**[19] and **7** → 84.7%, 7:4 ratio of **8**:**9**[19]), which could not be separated by column chromatography, $[\alpha]_D$ -42.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) for **8**[20]: δ 7.3-7.7 (m, 10H, 2 Ph); 5.93 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1); 4.72 (br, 1H, OH); 4.53 (d, 1H, H-2); 4.33 (d, 1H, $J_{3,4}$ = 2.6 Hz, H-3); 4.25 (dd, 1H, $J_{4,5}$ = 8.5 Hz, H-4); 4.02 (dd, 1H, $J_{5,6a}$ = 3.0 Hz, $J_{6a,6b}$ = 10.9 Hz, H-6a); 3.89 (dd, 1H, $J_{5,6b}$ = 5.9 Hz, H-6b); 3.80 (qq, 1H, H-5); 1.32, 1.47 (2s, 2x3H, CMe_2); 1.10 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 111.9 (s, CMe_2); 104.9 (s, C-1); 85.0 (s, C-2); 78.1 (s, C-4); 75.1 (s, C-3); 64.4 (s, C-6); 61.0 (s, C-5); 26.7 [s, $C(CH_3)_3$]; 26.7, 26.9 [2s, $C(CH_3)_2$]; 19.2 [s, $C(CH_3)_3$]. ^{1}H NMR ($CDCl_3$) for **9**[18] δ 7.3-7.7 (m, 10H, 2 Ph); 6.03 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1); 4.86 (t, 1H, $J_{5,6}$ = 6.5 Hz, H-5); 4.72 (br, 1H, OH); 4,47 (d, 1H, H-2); 4.45 (s, 1H, H-3); 4.40 (d, 2H, $J_{5,6}$ = 6.5

Hz, H-6a,6b); 1.37, 1.28 (2s, 2x3H, CMe_2); 1.07 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 155.9 (s, C-4); 114.0 (s, CMe_2); 106.9 (s, C-1); 103.05 (s, C-5); 84.1 (s, C-2); 74.8 (s, C-3); 58.7 (s, C-6); 26.7 [s, $C(CH_3)_3$]; 26.2 26.9 [2s, $C(CH_3)_2$]; 19.2 [s, $C(CH_3)_3$].

Conventional benzoylation using benzoyl chloride and pyridine, gave, after column chromatography (hexane-EtOAc, 9:1), 5-azido-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose, $[\alpha]_D$ -10.9° ($CHCl_3$) [lit.[10] $[\alpha]_D$ -10.5° ($CHCl_3$)], and 3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-α-D-*threo*-hex-4-enofuranose, $[\alpha]_D$ -22° (*c* 1.0, $CHCl_3$) [lit.[10] $[\alpha]_D$ -21° ($CHCl_3$)].

The mixture of **8** and **9** (3.1 g) was dissolved in dry dichloromethane (20 mL) and pyridinium dichromate (0.5 g), freshly activated 3A molecular sieve powder (0.8 g) and anhydrous acetic acid (0.25 mL) were added. The mixture was stirred at room temperature for ~4.5 h, filtered through Hyflo Super Cel and concentrated. Flash-column chromatography (hexane-EtOAc, 6:1) of the colourless syrup gave pure **10** (1.26 g, 42.5%, from **6**, and 1.34 g, 57.8% from **7**), $[\alpha]_D$ +30.2° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.4-7.7 (m, 10H, 2 Ph); 6.08 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1); 4.44 (s, 1H, H-4); 4.35 (d, 1H, H-2); 3.8-3.9 (m, 3H, H-5,6a,6b), 1.40, 1.44 [2s, 6 H, $C(CH_3)_2$]; 1.05 [s, 9 H, $C(CH_3)_3$]. ^{13}C NMR. δ 207.8 (s, C-3); 114.3 (s, CMe_2); 103.4 (s, C-1); 78.9 (s, C-2/C-4); 76.8 (s, C-4/C-2); 64.6 (s, C-6); 61.9 (s, C-5); 27.2, 27.5 [2s, $C(CH_3)_2$]; 26.8 (s, $C(CH_3)_3$]; 19.1 (s, CMe_3). *m/z*: 453 (M^+-15, 0.3%), 424 (10%), 381 (10%), 323 (14%), 253 (36%), 199 (100%), 153 (51%), 135 (70%).

Anal. Calcd for $C_{25}H_{31}N_3O_5Si$ (481.63): C 62.35, H 6.49, N 8.72. Found: C 62.56, H 6.78, N 8.56.

5-Azido-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethylene-1,2-*O*-isopropylidene-α-D-*ribo*-hex-3-enofuranose (11a, and 11b). (Ethoxylcarbonyl-methylene)triphenylphosphorane[14] (2.2 g, 1.2 equiv) was added to a solution of **10** in dry dichloromethane (8 mL) at 0 °C. The solution was stirred for ~40 min and then allowed to rise to room temperature. After about 7 h, TLC (hexane-EtOAc, 4:1) revealed the presence of a major and a minor fast-moving products. The solution was poured into ice-water and extracted with dichloromethane (3 x 100 mL). The extract was dried ($MgSO_4$) and concentrated, and eluted (hexane-EtOAc, 6:1) from silica gel to give, first, the *Z*-isomer **11a** (1.96g, 67.4%) $[\alpha]_D$ +80.8° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.3-7.7 (m, 10H, 2 Ph); 6.11 (t, 1H, $J_{2,3'} = J_{3',4}$ = 1.7 Hz, H-3'); 5.78 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1); 5.67 (td, 1H, $J_{2,4}$ 1.5 Hz, H-2); 4.82 (td, 1H, $J_{4,5}$ = 6.3 Hz, H-4); 4.24 (dd, 1H, $J_{3a'',3b''}$ = 14.2 Hz, $J_{3a'',3''}$ = 7.1 Hz, H-3a''); 4.12 (dd, 1H, $J_{3b'',3''}$ = 7.1 Hz, H-3b''); 3.87 (d, 2H, $J_{5,6}$ = 5.7 Hz, H-6a,6b); 3.56 (dd, 1H, H-5);

1.40, 1.44 [2s, 6 H, $C(CH_3)_2$]; 1.32 (t, 3H, H-3'''); 1.07 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR. δ 164.8 (s, C=O); 154.9 (s, C-3'); 117.7 s, C-3); 112.95 (s, CMe_2); 104.8 (s, C-1); 78.4 (s, C-2/C-4); 78.1 (s, C-4/C-2); 65.4 (s, C-6); 63.8 (s, C-5); 60.8 (s, C-3"); 27.2, 27.3 [2s, $C(CH_3)_2$]; 20.6 [s, $C(CH_3)_3$]; 19.1 (s, CMe_3); 14.1 (s, C-3'''). *m/z*: 536 (M^+-15, 5%), 494 (15%), 436 (75%), 240 (57%), 238 (46%), 227 (41%), 208 (34%), 199 (100%), 181 (37%), 169 (72%), 135 (64%), 113 (38%), 91 (40%).

Anal. Calcd for $C_{29}H_{37}N_3O_6Si$ (551.72): C 63.13, H 6.76, N 7.62. Found: C 63.56, H 6.78, N 7.28.

Eluted second was the *E*-isomer **11b** (0.32 g, 11.0%), $[\alpha]_D$ +71.6° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.3-7.8 (m, 10H, 2 Ph); 6.02 (t, 1H, $J_{2,3'}$ = 1.8 Hz, $J_{3',4}$ = 2.2 Hz, H-3'); 5.83 (d, 1H, $J_{1,2}$ = 4.7 Hz, H-1); 5.64 (d, 1H, H-4); 5.02 (dd, 1H-2); 4.0-4.1 (m, 2 H, H-3a",3"); 3.9-4.0 (m, 1H, H-5); 3.77 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6a); 3.54 (dd, 1H, $J_{5,6b}$ = 8.2 Hz, H-6b); 1.33, 1.39 [2s, 6H, $C(CH_3)_2$]; 1.22 (t, 3H, $J_{3''',3'''}$ = 7.1 Hz, H-3'''); 1.07 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR. δ 165.1 (s, C=O); 157.8(s, C-3'); 118.1 (s, C-3); 113.4 (s, CMe_2); 104.1 (s, C-1); 81.7/80.4 (s, C-2/C-4); 80.4/81.7 (s, C-4/C-2); 67.1 (s, C-6); 63.7 (s, C-5); 60.8 (s, C-3"); 26.6, 27.8 [2s, $C(CH_3)$]; 26.7 [s, $C(CH_3)_3$]; 19.1 (s, CMe_3); 14.1 (s, C-3'''). m/z: 536 (M^+-15, 3%), 494 (13%), 408 (19%), 362 (13%), 335 (23 (23%) 334 (60%), 240 (26%), 238 (16%), 227 (32%), 208 (16%), 199 (100%), 183 (14%), 169 (38%), 135 (66%), 113 (38%), 91 (27%).

Anal. Calcd for $C_{29}H_{37}N_3O_6Si$ (551.72): C 63.13, H 6.76, N 7.62. Found: C 63.45, H 6.78, N 7.46.

3,6-Anhydro-5-azido-5-deoxy-3-*C*-ethoxycarbonylmethyl-1,2-*O*-isopropylidene-α-D-glucofuranose (12). A solution of **11** (0.8 g) in dry tetrahydrofuran (20 mL) was treated with tetra-*n*-butylammonium fluoride (0.6 g, ~2 equiv) at room temperature under argon. TLC (hexane-EtOAc, 2:1) showed only one slower moving spot after 5 h. The solution was poured into cold satd aq $NaHCO_3$ (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined extract was concentrated and eluted from a short column of silica gel (hexane-EtOAc, 5:1), to afford **12** (0.37 g, 78.8%), $[\alpha]_D$ +30.5° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 5.94 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1); 4.76 (d, 1H, $J_{4,5}$ = 3.9 Hz, H-4); 4.66 (d, 1H, H-2); 4.17 (q, 2H, $J_{3'',3'''}$ = 7.1 Hz, H-3a",3b"); 4.16 (t, 1H, $J_{6a,6b}$ = 8.5, $J_{5,6b}$ = 7.6 Hz, H-6b); 3.94 (qq, 1H, $J_{5,6a}$ = 9.7 Hz, H-5); 3.73 (dd, 1H, H-6a); 2.91 (d, 1H, $J_{3a',3b'}$ = 15.8 Hz, H-3b'); 2.86 (d, 1H, H-3a'); 1.36, 1.52 [2s, 6H, $C(CH_3)_2$];1.28 (t, 3H, H-3'''). ^{13}C NMR. δ 113.4 (s, CMe_2); 106.5 (s, C-1); 91.5 (s, C-3); 86.3 (s, C-2); 85.6 (s, C-4); 68.7 (s, C-6); 60.9 (2s, C-3",5); 37.6 (s,

C-3'); 27.0, 27.6 (2s, CMe_2); 12.2 (s, C-3'''). *m/z*: 298 (M^+-15, 12%), 227 (11%), 199 (19%), 182 (11%), 171 (11%), 155 (50%), 153 (12%), 140 (19%), 124 (15%), 96 (44%), 43 (100%).

Anal. Calcd for $C_{13}H_{19}N_3O_6$ (313.31): C 49.84, H 6.11, N 13.41. Found: C 50.07, H 5.96, N 13.62.

3,6-Anhydro-1-deoxy-3-*C*-ethoxycarbonylmethylnojirimycin (4). A solution of **12** (0.72 g) in water (10 mL) was shakened with Amberlite 120 (H^+) resin (1.0 g) for 26 h at 40 °C when TLC (hexane-ethyl acetate, 1:1) showed a slow moving spot. The solution was filtered, diluted with ethanol (15 mL) and hydrogenated (50 psi) in the presence of 20% palladium hydroxide-on-charcoal (0.76 g) for 5.5 h at room temperature. The solution was filtered, concentrated and flash-column chromatography (EtOAc-MeOH, 2:1) of the syrupy residue gave **4** (0.13 g, 24.4%), $[\alpha]_D$ -7.6° (*c* 1.0, water). ^{1}H NMR (D_2O) δ 4.20 (q, 2H, $J_{3'',3'''}$ = 7.2 Hz, H-3a'',3b''); 4.14 (d, 1H, $J_{4,5}$ = 2.8 Hz, H-4); 4.1-4.3 (m, 2H, H-6a); 3.88 (d, 1H, $J_{1a,2}$ = 4.2 Hz, H-2); 3.8-3.9 (m, 2H, H-5); 3.7-3.8 (m, 1H, H-6b); 3.48 (dd, 1H, $J_{1a,1b}$ = 14.8 Hz, $J_{1a,2}$ = 4.2 Hz, H-1a); 3.21 (d, 1H, H-1b); 2.96 (d, 1H, $J_{3a',3b'}$ = 14.9 Hz, H-3a'); 2.85 (d, 1H, H-3b'); 1.26 (t, 3H, H-3'''). ^{13}C NMR δ 174.6 (C=O); 78.6 (s, C-3); 75.3 (s, C-6); 72.8 (s, C-2); 68.8 (s, C-4); 64.7 (s, C-3''); 58.8 (s, C-5); 40.7 (s, C-3'); 16.0 (s, C-3'''). *m/z*: 213 (M^+-18, 65%), 186 (63%), 155 (75%), 153 (25%), 126 (22%), 96 (42%), 56 (100%).

Anal. Calcd for $C_{10}H_{17}NO_5$ (231.25): C 51.92, H 7.41, N 6.06; found: C 52.12, H 7.17, N 5.87.

Benzoylation of 3,6-anhydro-1-deoxy-3-*C*-ethoxycarbonylmethylnojirimycin (13a,b). Compound **4** (77 mg) was dissolved in cold pyridine (2 mL) and treated, dropwise, with benzoyl chloride (0.23 mL). After 5 h at room temperature, the solution was poured into ice water and extracted with ethyl acetate, washed with water and concentrated. Flash-column chromatography (hexane-EtOAc, 1:1) of the residue gave a crystalline mixture (2:1)[17] of lactones **13a** and **13b** (99 mg, 76.1%), mp 136.5-138.5 °C, $[\alpha]_D$ -78.8 (*c* 1.0, chloroform). ^{1}H NMR ($CDCl_3$) for **13a** δ 5.42 (d, 1H, $J_{4,5}$ = 2.8 Hz, H-4); 5.2 (m, 1H, H-5); 4.58 (t, 1H, $J_{1a,2}$ = 7.5 Hz, $J_{1b,2}$ = 8.9 Hz, H-2); 4.40 (dd, 1H, $J_{5,6a}$ = 2.8 Hz, $J_{6a,6b}$ = 10.0 Hz, H-6a); 4.12 (dd, 1H, $J_{1a,1b}$ = 12.2 Hz, H-1a); 4.02 (d, 1H, H-6b); 3.77 (dd, 1H, H-1b); 3.17 (d, 1H, $J_{3a',3b'}$ = 17.8 Hz, H-3a'); 2.86 (d, 1H, H-3b'). ^{13}C NMR δ 171.8 (C=O); 80.9 (s, C-2/C-3); 80.5 (s, C-3/C-2); 74.5 (s, C-4); 72.6 (s, C-6); 52.6 (s, C-5); 45.2 (s, C-1); 34.1 (s, C-3'). ^{1}H NMR ($CDCl_3$) for **13b** δ 4.9-5.0 (m, 1H, H-4); 4.8-4.9 (m, 2H, H-2,5); 4.58 (dd, 1H, $J_{1a,1b}$ = 13.8 Hz, $J_{1a,2}$ = 7.7 Hz, H-1a); 4.26 (dd, 1H, $J_{5,6a}$ = 5.9 Hz, $J_{6a,6b}$ = 10.0 Hz, H-6a); 4.20 (d, 1H, H-

6b); 3.71 (dd, 1H, $J_{1b,2}$ = 7.1 Hz, H-1b); 3.20 (d, 1H, $J_{3a',3b'}$ = 15.2 Hz, H-3a'); 2.83 (d, 1H, H-3b'). ^{13}C NMR. δ 1741.5 (C=O); 80.5 (s, C-2/C-3); 80.1 (s, C-3/C-2); 74.6 (s, C-4); 73.0 (s, C-6); 55.1 (s, C-5); 41.0 (s, C-1); 34.1 (s, C-3'). *m/z*: 393 (M^+, 34%), 288 (20%); 105 (100%).

Anal. Calcd for $C_{22}H_{19}NO_6$ (393.40): C, 67.17; H, 4.87; N, 3.56. Found: C, 66.97; H, 4.79; N, 3.18.

3,6-Anhydro-5-azido- (14) and 5-amino-5-deoxy-3-*C*-(2-hydroxyethyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (15). Lithium aluminium hydride (0.47 g) was added to a stirred ice-cold solution of **12** (1.28 g) in dry tetrahydrofuran (30 mL). The solution was then stirred at room temperature for 3 h under argon when TLC (hexane-EtOAc, 2:1) showed the presence of a fast (minor) and slow (major) moving compounds. Water (0.5 mL) was carefully added, followed by 10% aq sodium hydroxide (0.5 mL) and water (1.5 mL). The solution was filtered, concentrated and the syrupy residue chromatographed (hexane-EtOAc, 3:1) to give, first, **14** (0.143 g, 12.9%), $[\alpha]_D$ +35.1° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.96 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1); 4.59 (d, 1H, $J_{4,5}$ = 3.6 Hz, H-4); 4.54 (d, 1H, H-2); 4.18 (t, 1H, $J_{5,6a}$ = 7.7 Hz, $J_{6a,6b}$ = 8.2 Hz, H-6a); 3.87 (m, 3H, H-3a",3b",5); 3.78 (dd, 1H, $J_{5,6b}$ = 9.6 Hz, H-6b); 2.12 (qq 1H, $J_{3a',3b'}$ = 14.6 Hz, $J_{3a',3a"}$ = 4.1 Hz, $J_{3a',3b"}$ = 6.1 Hz, H-3a'); 1.82 (qq, 1H, $J_{3b',3a"}$ = 8.0 Hz, $J_{3b',3b"}$ = 4.6 Hz, H-3b'). 1.60 (br s, 1H, OH); 1.52, 1.36 [2s, 2x3H, $C(CH_3)_2$]. ^{13}C NMR. δ 113.4 (s, CMe_2); 107.0 (s, C-1); 93.9 (s, C-3); 86.3 (s, C-2); 85.6 (s, C-4); 68.5 (s, C-3"); 61.1 (s, C-5); 59.1 (s, C-6), 33.9 (s, C-3'); 27.6, 27.0 [2s, $C(CH_3)_2$].

Anal. Calcd for $C_{11}H_{17}N_3O_5$: C, 48.69; H, 6.32; N, 15.49. Found: C, 49.12; H, 5.97; N, 14.98.

Elution using EtOAc-MeOH (3:1) then gave **15** (.66 g, 65.9%), $[\alpha]_D$ +33.1° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.90 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1); 4.54 (d, 1H, $J_{4,5}$ = 3.5 Hz, H-4); 4.30 (d, 1H, H-2); 4.09 (t, 1H, $J_{5,6a}$ = 7.7 Hz, $J_{6a,6b}$ = 8.3 Hz, H-6a); 3.88 (qq, 1H, $J_{3a',3a"}$ = 4.1 Hz, $J_{3b',3a"}$ = 8.2 Hz, $J_{3a",3b"}$ = 10.9 Hz, H-3a"); 3.79 (qq, 1H, $J_{3a',3b"}$ = 6.0 Hz, $J_{3b',3b"}$ = 4.7 Hz, H-3b"); 3.62 (qq, 1H, $J_{4,5}$ = 3.5 Hz, $J_{5,6a}$ = 7.7 Hz, $J_{5,6b}$ = 10.1 Hz, H-5); 3.39 (dd, 1H, H-6b); 2.20 (br s, 3H, OH, NH_2); 2.10 (qq, 1H, $J_{3a',3b'}$ = 14.5 Hz, H-3a'); 1.83 (qq, 1H, H-3b'); 1,51, 1.36 [2s, 2x3H, $C(CH_3)_2$]. ^{13}C NMR. δ 113.0 (s, CMe_2); 106.5 (s, C-1); 93.2 (s, C-3); 86.95 (s, C-2/C-4); 85.05 (s, C-4/C-2); 72.25 (s, C-3"); 58.8 (s, C-5); 54.9 (s, C-6); 34.0 (s, C-3'); 27.5, 26.9 [2s, $C(CH_3)_2$]. *m/z*: 245 (M^+, 6%), 230 (M^+-15, 5%) 186 (11%), 129 (24%), 158 (14%), 157 (100%), 110 (15%), 97 (12%), 59 (61%), 43 (89%).

Anal. Calcd for $C_{11}H_{19}NO_5$ (245.28): C, 53.87; H, 7.81; N, 5.71. Found: C, 53.66; H, 7.70; N, 5.32.

3,6-Anhydro-1-deoxy-3-(2-hydroxyethyl)nojirimycin (5). A solution of **14** (0.14 g) in water (5 mL) was stirred with Amberlite IR 120 (H^+) resin (0.2 g) at 40 °C for 31 h. The solution was filtered, diluted with ethanol (20 mL), and treated with 20% palladium hydroxide-on-charcoal (0.15 g) in the presence of hydrogen (50 psi) for 6.5 h. The solution was filtered, concentrated and flash-column chromatography (EtOAc-MeOH, 1:1) gave **5** (33 mg, 34.9%), $[\alpha]_D$ +9.8° (*c* 1.0, MeOH). ^{1}H NMR ($CDCl_3$-D_2O) δ 4.07 (d, 1H, $J_{4,5}$ = 3.7 Hz, H-4); 4.06 (dd, 1H, $J_{5,6a}$ = 3.6 Hz, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.02 (d, 1H, H-6b), 3.77 (t, H, $J_{3',3a''}$ = $J_{3a'',3b''}$ = 7.1 Hz, H-3a"); 3.6-3.7 (m, 2H, H-2,3b"); 3.50 (t, 1H, $J_{4,5}$ = 3.7 Hz, H-5); 3.27 (dd, $J_{1a,2}$ = 3.8 Hz, $J_{1a,1b}$ = 15.0 Hz, $J_{1a,2}$ =3.8 Hz, Hz, H-1a); 1.9-2.2 (m, 2H, H-3a',3b'); 2.93 (d, 1 H, H-1b). ^{13}C NMR ($CDCl_3$-D_2O) δ 79.4 (s, C-3); 76.2 (s, C-2); 74.25 (s, C-4); 69.9 (s, C-6); 59.2 (s, C-3"); 58.4 (s, C-5); 47.9 (s, C-1); 37.4 (s, C-3'). *m/z*: 189 (M^+, 5%), 171 (63%), 142 (84%), 113 (100%), 95 (57%), 43 (82%).

Anal. Calcd for $C_8H_{15}NO_4$ (189.21): C, 50.78; H, 7.99; N, 7.40. Found: C, 51.12; H, 7.65; N, 7.57.

Similar treatment of **15** also gave **5** (15.3%), identical to that obtained above.

5-Bromo-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-β-L-*lyxo*-hexos-3-ulofuranose (16). 5-Bromo-6-*O*-*tert*-butyldiphenylsilyl-5-dideoxy-1,2-O-isopropylidene-β-L-idofuranose[10] (0.91 g) was treated with pyridinium dichromate-acetic acid as for **8** to give, after flash-column chromatography (hexane:EtOAc, 5:2), **16** (0.71 g, 81.2%), $[\alpha]_D$ +58.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.3-7.7 (m, 10H, 2 Ph); 6.20 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1); 4.99 (s, 1H, $J_{2,4}$ <1 Hz, H-4); 4.41 (d, 1H, H-2); 3.8-4.2 (m, 3H, H-5,6a,6b); 1.44, 1.49 ([s, 2x3H, $C(CH_3)_2$]; 1.05 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 208.7 (s, C-3); 114.5 (s, CMe_2); 103.85 (s, C-1); 78.0 2/C-4); 76.3 (s, C-4/C-2); 64.0 (s, C-6); 51.0 (s, C-5); 27.2, 27.5 [2s, $C(CH_3)_2$]; 26.7 (s, $C(CH_3)_3$]; 19.2 (s, CMe_3). *m/z*: 463,461 (1:1, M^+-15, 23%); 335 (49%); 263, 261 (1:1, 57%); 253 (40%); 199 (100%).

Anal. Calcd for $C_{25}H_{31}BrO_5Si$ (519.51): C, 57.80; H, 6.01; Br, 15.40. Found: C, 57.60; H, 6.41; Br, 15.72.

(3*E*)-5-Bromo-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethylene-1,2-*O*-isopropylidene-β-L-*lyxo*-hex-3-enofuranose (17). Compound **16** (90 mg) was reacted with (ethoxylcarbonylmethylene)triphenylphosphorane[14] (70 mg, 1.2 equiv) as for **11**, to give only the 3*Z*-isomer **17** (77 mg, 75.4%), $[\alpha]_D$ +62.3° (*c* 1, chloroform). ^{1}H NMR ($CDCl_3$) δ 7.3-7.7 (m, 10H, 2 Ph); 6.02 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1); 5.82 (t, 1H, $J_{2,3'}$ = $J_{3',4}$ = 1.7 Hz, H-3'); 5.70 (d, 1H, H-2); 5.40 (s, 1H, H-4); 4.26 (q, 2H, $J_{3a'',3b''}$ =14.1 Hz, H-3a', H-3b"); 4.06 (t,

1H, $J_{5,6a}$ = 7.0 Hz, $J_{5,6b}$ = 8.7 Hz, H-5); 3.9-4.0 (m, 2H, J6a,6b); 1.45, 1.48 [2s, 2x3H, $C(CH_3)_2$]; 1.37 (t, 3H, $J_{3'',3'''}$ =7.1 Hz, H-3'''); 1.06 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR ($CDCl_3$) δ 164.65 (s, C=O); 156.8 (s, C-3'); 116.9 (s, C-3), 113.2 [s, CMe_2]; 106.2 (s, C-1); 78.9 (s, C-2/C-4), 78.7 (s, C-4/C-2); 64.7 (s, C-6); 60.85 (s, C-3''); 55.8 (s, C-5); 26.8, 26.9 [2s, $C(CH_3)_2$]; 26.8 [s, $C(CH_3)_3$]; 19.3 (s, CMe_3); 14.5 (s, C-3'''). *m/z*: 573, 575 (1:1, M^+-15, 2%), 475 (20%), 473 (25%), 261 (8%), 241 (7%), 199 (100%), 169 (4%).

Anal. Calcd for $C_{29}H_{37}BrO_6Si$ (589.61): C, 59.08; H, 6.32; Br, 13.55. Found: C, 58.72; H, 6.49; Br, 13.56.

5-Bromo-6-*O*-*tert*-butyldiphenylsilyl-3,5-dideoxy-3-*C*-ethoxycarbonylmethyl-1,2-*O*-isopropylidene-β-L-talo- (18) and ido-furanose (19). A solution of **17** (0.64 g) in ethanol (25 mL) was shaken with 10% palladium-on-charcoal (0.8 mg) under hydrogen (50 psi) for 6 h when TLC (hexane-EtOAc, 5:1) showed a fast (major) and a slow (minor) moving spot. The solution was filtered, concentrated and eluted (hexane-EtOAc, 7:1) from a column of silica gel to give, first, **18** (0.30 g, 40%), $[\alpha]_D$ +17.9° (*c* 1.1, chloroform). ^1H NMR ($CDCl_3$) δ 7.3-7.7 (m, 10H, 2 Ph); 5.85 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1); 4.80 (t, 1H, $J_{2,3}$ = 4.2 Hz, H-2); 4.17 (q, 2H, $J_{3'',3'''}$ = 7.2 Hz, H-3a",3b"); 4.1-4.2 (m, 2H, H-3,4); 3.9-4.1 (m, 3H, H-5,6a,6b); 2.67 (dd, 1H, $J_{3a',3b'}$ = 16.3 Hz, $J_{3,3a'}$ = 9.8 Hz, H-3a); 2.31 (dd, 1H, $J_{3,3b}$ = 4.3 Hz, H-3b); 1.33, 1.47 [2s, 2x3H, $C(CH_3)_2$]; 1.29 (t, 3H, H-3'''); 1.05 (s, 9H, $C(CH_3)_3$]. ^{13}C NMR ($CDCl_3$) δ 172.2 (s, C=O); 117.7 (s, CMe_2); 105.9 (s, C-1); 81.2 (s, C-2/C-4); 79.2 (s, C-4/C-2); 77.2 (s, C-6); 60.6 (s, C-3'''); 44.9 (s, C-5); 41.0 (s, C-3); 29.5 (s, C-3'); 26.9 (s, $C(CH_3)_3$]; 26.5, 5.5 (2s, $C(CH_3)_2$]; 19.2 (s, CMe_3); 14.2 (s, C-3'''). *m/z*: 575, 577 (M^+-15, 6%,), 533, 535 (1:1, 7%); 475, 477 (1:1, 40%); 395 (18%), 263 (31%); 261 (37%); 200 (23%); 199 (100%); 197 (26%); 171 (21%); 135 (29%).

Anal. Calcd for $C_{29}H_{39}BrO_6Si$ (591.61): C, 58.88; H, 6.64; Br, 13.51. Found: C, 58.67; H, 6.88; Br, 13.23.

Eluted second was **19** (0.17 g, 25%), $[\alpha]_D$ -6.3° (*c* 1.0 chloroform). ^1H NMR ($CDCl_3$) δ 7.3-7.7 (m, 10H, 2 Ph); 5.81 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1); 4.71 (t, 1H, $J_{2,3}$ = 5.0 Hz, H-2); 4.5 (m, 1H, H-3); 4.1-4.2 (m, 1H, H-5); 4.12 (dd, $J_{3,4}$ = 1.9 Hz, $J_{4,5}$ = 7.2 Hz, H-4); 4.1-4.2 (m, 4H, H-3a",3b"6a,6b); 2.4-2.6 (m, 2H, H-3a',3b'); 1.45 [2s, 2x3H, $C(CH_3)_2$]; 1.27 (t, 3H, $J_{3'',3'''}$ = 7.1 Hz, H-3'''); 1.27 [s, 6H, $C(CH_2)_2$]; 1.04 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR ($CDCl_3$) δ 171.65 (s, C=O); 112.0 (s, CMe_2); 105.0 (s, C-1); 81.2 (s, C-2); 77.9 (s, C-4); 65.3 (s, C-6); 60.8 (s, C-3'''); 54.3 (s, C-5); 42.9 (s, C-3); 29.9 (s, C-3'); 26.8 (s, $C(CH_3)_3$]; 26.6, 26.5 (2s, $C(CH_3)_2$]; 19.2 (s, CMe_3); 14.7 (s, C-3'''). *m/z*: 533, 535 (1:1, 2%), 455 (7%), 409 (9%); 398

(19%), 397 (57%), 340 (22%), 339 (87%), 255 (20%), 227 (40%), 211 (10%), 200 (13%), 199 (100%), 197 (10%), 183 (26%), 177 (9%); 141 (25%), 135 (30%).

Anal. Calcd for $C_{29}H_{39}BrO_6Si$ (591.61): C, 58.88; H, 6.64; Br, 13.51. Found: C, 58.52; H, 6.34; Br, 13.72.

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REFERENCES AND NOTES

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19. The product yields were estimated from their ^{13}C NMR spectrum and from products obtained after benzoylation; for estimation from their ^{13}C NMR spectrum, carbons 1, 2, 3 and 6 were compared.
20. ^{1}H and ^{13}C NMR assignments were made by comparison with spectra of pure samples obtained by debenzoylation of the pure benzoyl derivatives.