trophotometer. NMR spectra were determined on a Bruker WM-250 spectrometer in $CDCl_3$ solutions with Me_4Si as internal reference (δ 0). Nuclear Overhauser effect was determined with the aid of an Aspect 2000 microprogram which allowed direct accumulation of NOE difference FIDs on a sample degassed by bubbling Ar through the solution for 40 min.

Mass spectra were taken on AEI 902 instrument. Optical rotations were measured with a Perkin Elmer 141 polarimeter with a 10-cm microcell.

Extraction. Sponge (*Axinella cannabina*), collected in the Bay of Taranto, near Porto Cesareo in Autumn 1983 (350 g, dry after extraction), was homogenized and extracted four times with CH_3OH at room temperature for 3 days. The combined extracts (5 L) were concentrated under red press and the remaining aqueous residue was extracted with $CHCl_3$. The organic phase was taken to dryness leaving an oily residue (15 g) which was chromatographed on a SiO_2 (900 g) column under pressure, using as eluent solvent mixtures in increasing polarities from 40–70 °C light petroleum to Et_2O through benzene. Elution with 40–70 °C light petroleum–benzene (8:2), 40–70 °C light petroleum–benzene (2:8), and Et_2O afforded fractions A (1.6 g), B (5 g), and C (300 mg) respectively, which were used for the isolation of 1–6 as described below.

Isolation of 2 and 5. Fraction A (1.6 g), obtained as above, was rechromatographed on a silica gel column (100 g), eluent 40–70 °C light petroleum, to give 300 mg of an oily residue containing a mixture of isothiocyanates, which were separated by HPLC (LiChrosorb Si 60, *n*-hexane), thus obtaining 18 mg of **2** and 20 mg of **5**: $[\alpha]_D$ + 41.0 (*c* 0.35, $CHCl_3$); HRMS, *m/z* 263.1701, $C_{16}H_{25}NS$ requires 263.1709; ν_{max} 2100, 1640, 895 cm^{-1}; δ 5.04 and 4.64 (1 H each, narrow ms), 4.09 (1 H, dd, *J* = 11.5 and 5.0 Hz), 2.33 (1 H, bd, *J* = 11.5 Hz), 2.05 (1 H, octet, *J* = 6.5 Hz), 1.86 (1 H, m), 1.14 and 1.01 (3 H each, ds, *J* = 6.5 Hz), and 0.80 (3 H, s). **2**: $[\alpha]_D$ −24.4 (*c* 0.28, $CHCl_3$); HRMS, *m/z* 263.1706, $C_{16}H_{25}NS$ requires 263.1709; ν_{max} 2100, 1640, 895 cm^{-1}; δ 4.95 and 4.92 (1 H each, narrow ms), 3.46 (1 H, t, *J* = 10.5 Hz), 1.77 (3 H, bs), 1.14 (3 H, d, *J* = 6.5 Hz), and 0.86 (3 H, s).

Isolation of 1 and 4. Rechromatography of fraction B (5 g), obtained as above, with 40–70 °C light petroleum–benzene 8:2 on a silica gel column (400 g), gave an oily product (503 mg), which was further purified by HPLC (μ-bondapack C_{18}, eluent 20% H_2O in CH_3OH), thus affording 20 mg of **4** [$[\alpha]_D$ +39.6 (*c* 0.30, $CHCl_3$); ν_{max} 2135, 1640 and 895 cm^{-1}; HRMS, *m/z* 231.1985, $C_{16}H_{25}N$ requires 231.1988; δ 5.05 and 4.72 (1 H, narrow ms), 3.91 (1 H, ddt, *J* = 11.5, 5.0, and 2.5 Hz), 2.34 (1 H, d, *J* = 11.5 Hz), 2.18 (1 H, octet, *J* = 6.5 Hz), 2.03 (1 H, m), 1.16 (3 H, d, *J* = 6.5 Hz), 1.04 (3 H, d, *J* = 6.5 Hz), 0.79 (3 H, s)] and 22 mg of **1** [$[\alpha]_D$ −42.3 (*c* 0.53, $CHCl_3$)], which was identical in all aspects with authentic sample.[7]

Isolation of 3 and 6. Fraction C (300 mg), obtained as above, was chromatographed on a silica gel column (80 g, eluent Et_2O), thus obtaining a mixture of **3** and **6**, which was resolved into the individual components by HPLC (LiChrosorb Si 60, EtOAc). **3** (4 mg): $[\alpha]_D$ −24.0 (*c* 0.30, $CHCl_3$); ν_{max} 3440 and 1680 cm^{-1}; HRMS, *m/z* 249.2089, $C_{16}H_{27}NO$ requires 249.2094. Cis isomer: δ 7.99 (d, *J* = 2.2 Hz), 4.88 (1 H, b), 4.70 and 4.64 (1 H each, narrow ms), 4.09 (1 H, q, *J* = 10.2 Hz), 1.70 (3 H, s), 0.95 (3 H, d, *J* = 6.5 Hz), 0.93 (3 H, s). Trans isomer: δ 7.77 (d, *J* = 12.4 Hz), 5.13 (1 H, b), 4.86 and 4.74 (1 H each, narrow ms), 3.26 (1 H, q, *J* = 10.2 Hz), 1.68 (3 H, s), 0.91 (3 H, s), and 0.85 (3 H, d, *J* = 6.5 Hz). **6** (3.5 mg): $[\alpha]_D$ +48.5 (*c* 0.30, $CHCl_3$); ν_{max} 3440 and 1675 cm^{-1}; HRMS, *m/z* 249.2086, $C_{16}H_{27}NO$ requires 249.2094. Cis isomer: 8.08 (1 H, d, *J* = 1.5 Hz), 5.30 (1 H, b), 4.89 and 4.43 (1 H each, narrow ms), 4.22 (1 H, ddd, *J* = 11.2, 9.0, and 4.5 Hz), 1.00 and 0.95 (3 H each, ds, *J* = 6.5 Hz), and 0.84 (3 H, s).

Treatment of 1 with Sulfur To Obtain 2. Compound **1** (5 mg) and excess S were heated at 120 °C for 16 h; after addition of 40–70 °C light petroleum (5 mL) and filtration, the solution was taken to dryness and the residue was purified by TLC (silica gel, *n*-hexane). The band R_f 0.6, scraped and eluted with Et_2O, afforded 3 mg of an oily product, which was identical with natural **2** on the basis of their chromatographic and spectral properties.

Treatment of 4 with Sulfur To Obtain 5. This was analogous to the preparation of **2** from **1** above. From 5 mg of **4**, 4 mg of crude **5** were obtained. After purification by TLC (SiO_2, *n*-hexane), its spectral and chromatographic properties matched those of natural **5**.

Hydration of 1 To Obtain 3. A solution of **1** (12 mg) in anhydrous Et_2O (6 mL) and AcOH (5 mL) was kept at room temperature for 2 h. After washing with 10% aqueous Na_2CO_3 and then with H_2O, the organic phase was dried and taken to dryness, thus giving a residue which was chromatographed on TLC (SiO_2, Et_2O); the band R_f 0.5, eluted with Et_2O, gave a compound (7.5 mg), which was identical with natural **3** by comparison of spectral and chromatographic data.

Hydration of 4 To Give 6. Compound **4** (8 mg) was treated with AcOH (5 mL) in anhydrous Et_2O (6 mL) by the procedure used for **1**, thus **6** (4.5 mg) was obtained identical with **6** isolated from *A. cannabina*.

Dehydrogenation of 4 to Eudalene 7. A mixture of **4** (5 mg) and 10% Pd/C (10 mg) was heated at 280 °C under N_2 for 1 h. Extraction of the mixture with $CHCl_3$ and TLC (silica gel, *n*-hexane, UV) gave 2 mg of eudalene identified by comparison of its spectral properties with those of an authentic sample.

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Registry No. **1**, 54462-52-1; **2**, 91466-60-3; **3**, 91466-61-4; **4**, 91466-62-5; **5**, 91466-63-6; **6**, 91466-64-7; **7**, 490-65-3.

Regio- and Stereoselective Synthesis of Methyl α-L-Daunosaminide Hydrochloride

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Methyl 4-*O*-(trichloroacetamidoyl)-2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (**6**), prepared from methyl 2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (**5**), was cyclized to the iodooxazoline **7** which, by hydrolysis under acidic conditions, afforded the corresponding hydrochloride **8**. The deiodination reaction was performed with Bu_3SnH and methyl 3-amino-2,3,6-trideoxy-α-L-lyxopyranoside hydrochloride (methyl α-L-daunosaminide hydrochloride) **1** was obtained in 80% yield. The intermediate **5** was synthesized starting from methyl 4-*O*-mesyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside **3** in 80% yield by means of carbonate anion on polymeric support.

3-Amino-3-deoxyhexoses have been widely encountered as sugar moieties of biologically active substances. L-Daunosamine (3-amino-2,3,6-trideoxy-L-*lyxo*-hexose), in particular, is important as the carbohydrate constituent

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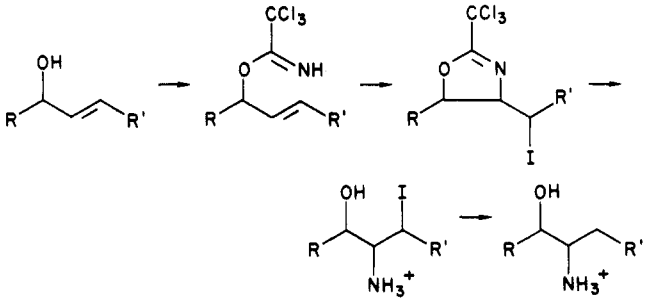
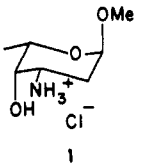
of the anthracycline antibiotics such as daunorubicin[1] and adriamycin,[2] both of which have strong antitumor activity. A number of syntheses of this amino sugar have been already reported,[3] giving evidence of the popularity of this target.

As a part of a program directed toward the synthesis of antibiotic sugars, we have recently developed new methods for the regio- and stereocontrolled conversion of allylic alcohols into iodo amino alcohols and the corresponding amino diols via iodocyclization of a trichloroacetimidate.[4]



We recently reported a new synthesis of methyl α-L-ristosaminide hydrochloride following this route.[5] We wish to report here a further application of this method to provide a stereoselective approach to methyl α-L-daunosaminide hydrochloride 1.[6] The required intermediate,



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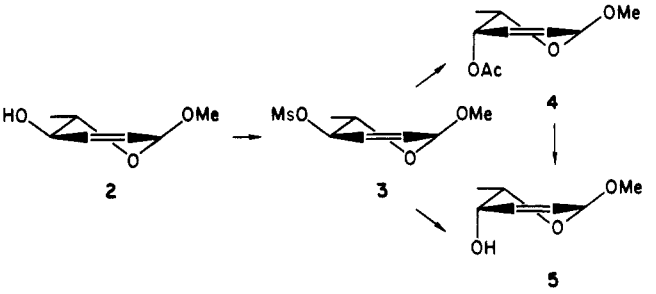
methyl 2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (5) was obtained from methyl 2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside 2.[7]

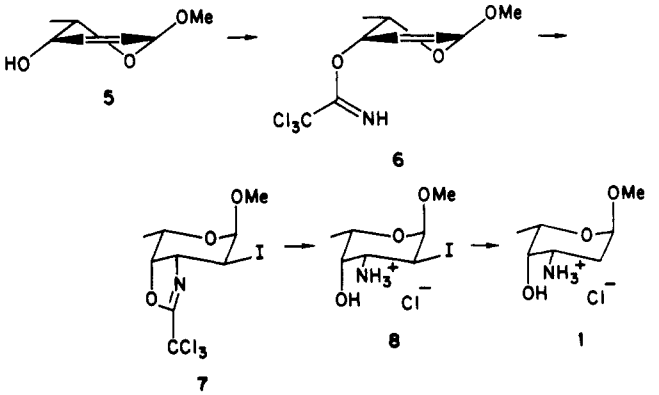
Since the crucial point of this conversion was the inversion at C-4, we have studied the problem in some detail. The esterification of alcohols with diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) was shown to proceed with inversion of configuration and was applied in carbohydrate chemistry.[8] As an alternative to the use of DEAD, we choose to perform the conversion of methyl 2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside 2 to 5 by a nucleophilic displacement of the mesyl derivative 3[9] by means of acetate anion on polymeric support (Amberlyst A 26).[10]

The acetate 4, obtained in 65% yield, was then hydrolyzed to 5 with Amberlyst A 26 in the OH^- form. To



improve the overall yield by a one-step process, we obtained directly 5 by treating the mesyl derivative 3 with an excess of Amberlyst A 26 in the CO_3^{2-} form.[11] Under these conditions, simply by filtering off the resin, 5 was obtained in 80% yield after purification by silica gel chromatography.

The compound 5 was then converted into the trichloroacetimidate 6 by a standard procedure[12] in 60% yield after silica gel chromatography. Iodocyclization of 6 to



iodooxazoline 7 was then performed with *N*-iodosuccinimide in $CHCl_3$, and the excess iodine and succinimide were simply removed by stirring with Amberlyst A 26 in the Cl^- form.[13]

The iodooxazoline 7, obtained in 95% yield, was subjected to the deiodination reaction with Bu_3SnH/AIBN. Since a complex mixture of products was observed due to the presence of C–Cl bonds susceptible to cleavage, 7 was quantitatively hydrolyzed to hydrochloride 8 with 2 N HCl. The cleavage of the C–I bond was then performed with Bu_3SnH/AIBN, and methyl α-L-daunosaminide hydrochloride 1 was obtained in 88% yield after silica gel chromatography. This product was eventually converted to the diacetyl derivative 9 in 80% yield, whose spectral data were in agreement with those reported in the literature.[1b]

Experimental Section

General Methods. Column chromatography was performed by a medium-pressure system using silica gel (Merck 60, 0.040–0.063 mm). Solvents used for elution were indicated in the

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(8) (a) Grynkiewicz G.; Burzynska, H. *Tetrahedron* **1976**, *32*, 2109. (b) Mitsunobo, O. *Synthesis* **1981**, 1. (c) In our hands this method led to 5 in 65% overall yield. After submission of this paper Pauls and Fraser-Reid (Pauls, H. W.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1031) by using the Mitsunobo method in a new synthesis of 1 reported the inversion of the C-4 hydroxy group of 2 with an overall yield of 89%.

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(11) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *Synthesis* **1981**, 793.

(12) (a) Overman, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 2901. (b) Yamamoto, Y.; Shimoda, H.; Oda, I.; Ynouye, Y., *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3247.

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text and are reported as volume percent. For reactions requiring dry solvents, tetrahydrofuran was distilled from sodium benzophenone ketyl. Pentane and chloroform were distilled from phosphorus pentoxide and stored over activated 3A molecular sieves. Melting points were determined in a silicone oil bath (Buchi 510) and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 682 spectrophotometer. Nuclear magnetic resonance (^{1}H NMR) spectra were determined with a Perkin Elmer R 12 B spectrometer (60 MHz) and a Varian XL 100 spectrometer (100 MHz). Chemical shift data are reported in δ (ppm) units relative to internal tetramethylsilane in $CDCl_3$ or CD_3OD or pyridine-d_5. Optical rotations were recorded on a Perkin Elmer 241 automatic polarimeter.

Methyl 4-*O*-Mesyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (3). To a solution of methyl 2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside **2** (1.44 g, 10 mmol) in dry CH_2Cl_2 (50 mL), containing triethylamine (1.52 g, 15 mmol) and a catalytic amount of (*N*,*N*-dimethylamino)pyridine (50 mg), was added mesyl chloride (1.26 g, 11 mmol) at 0 °C. After 0.5 h the organic phase was washed with H_2O and then with 5% aqueous $NaHCO_3$ and evaporated under vacuum; 2.0 g (90 %) of the mesyl derivative **3** were obtained as an oil: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 7 Hz), 3.0 (s, 3 H), 3.35 (s, 3 H), 3.6–4.1 (m, 1 H), 4.5–4.9 (m, 2 H), 5.6–6.1 (m, 2 H); $[\alpha]_D$ −140° (*c* 1.3, CH_2Cl_2). Anal. Calcd for $C_8H_{14}O_5S$: C, 43.24; H, 6.35. Found: C, 43.29; H, 6.34.

Methyl 4-*O*-Acetyl-2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (4). To a solution of **3** (2.2 g, 10 mmol) in benzene (20 mL) was added Amberlyst A 26 (AcO^-) (10 g, ~3.8 mequiv/g), and the suspension was refluxed for 12 h. The resin was then filtered off and the organic phase evaporated. Silica gel chromatography of the residue (cyclohexane:ethyl acetate 9:1) gave 1.3 g (65%) of **4** as an oil: IR (neat) 1740 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.15 (d, 3 H, J = 7 Hz), 2.0 (s, 3 H), 3.3 (s, 3 H), 4.1 (m, 1 H), 4.5–5.0 (m, 2 H), 5.8–6.1 (m, 2 H); $[\alpha]_D$ +136° (α:β = 8:2)(*c* 1, MeOH). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.95; H, 7.57.

Methyl 2,3,6-Trideoxy-α-L-*threo*-hex-2-enopyranoside (5) (Method A). A solution of **4** (3.0 g, 15 mmol) in methanol (30 mL) was stirred for 6 h at room temperature with Amberlyst A 26 (OH^-) (5 g, ~3.8 mequiv/g). The resin was then filtered off, and the solvent was evaporated under vacuum to give 1.94 g (90%) of **5** after silica gel chromatography (cyclohexane:ethyl acetate 8:2) as a viscous oil: ^{1}H NMR ($CDCl_3$) δ 1.3 (d, 3 H, J = 6 Hz), 2.65 (bs, 1 H, OH), 3.4 (s, 3 H), 3.3–3.8 (m, 1 H), 3.9–4.5 (dq, 1 H), 4.85 (d, 1 H, J = 3 Hz), 5.6–6.4 (m, 2 H); $[\alpha]_D$ +139° (*c* 2, MeOH). Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.27; H, 8.38.

Methyl 2,3,6-Trideoxy-α-L-*threo*-hex-2-enopyranoside (5) (Method B). To a solution of **3** (2.2 g, 10 mmol) in benzene (20 mL) was added Amberlyst A 26 (CO_3^{2-}) (10 g, ~3.8 mequiv/g), and the suspension was refluxed for 12 h. The resin was then filtered off and the organic phase evaporated. Silica gel chromatography (cyclohexane:ethyl acetate 9:1) gave 1.15 g (80%) of **5**, identical with the sample from A by ^{1}H NMR spectral data, optical rotation, and elemental analysis.

Methyl 4-*O*-(Trichloroacetimidoyl)-2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (6). A solution of **5** (2.16 g, 15 mmol) in dry THF (30 mL) under inert atmosphere was added at 0 °C to a stirred suspension of NaH (50% dispersion in mineral oil, 150 mg, 3 mmol, previously washed with dry pentane) in THF (20 mL). Stirring was continued for 1 h at room temperature, and the mixture was then added at 0 °C to a solution of trichloroacetonitrile (2.3 g, 16 mmol) in dry THF (20 mL). After 1.5 h the solvent was evaporated under vacuum and the residue dissolved in pentane (40 mL) containing methanol (1 mL). The solution was filtered, and the organic phase was removed under reduced pressure. By silica gel chromatography (pentane:ether 9:1) **6** (2.6 g, 60%) was obtained as a clear oil: IR (neat) 3350, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3 H, J = 6 Hz), 3.45 (s, 3 H), 4.0–4.5 (m, 1 H), 4.8–5.2 (m, 2 H), 5.8–6.5 (m, 2 H), 8.4 (bs. 1 H, C=NH); $[\alpha]_D$ +95° (*c* 0.9, CH_2Cl_2); MS, *m/e* 244 (M^+ − $CHOCH_3$), 215, 101, 72.

Methyl 2-Iodo-2,3,6-trideoxy-4-*O*,3-(3,3,3-trichloro-1-aza-1-propene-1,2-diyl)-α-L-galactopyranoside (7). To a solution of **6** (3.45 g, 12 mmol) in $CHCl_3$ (70 mL) at room temperature was added *N*-iodosuccinimide (2.9 g, 13 mmol) under stirring. After 8 h the excess iodine and succinimide were removed by adding dried Amberlyst A 26 (Cl^-) (20 g), solvent was removed under vacuum, and pure **7** (4.7 g, 95%) was obtained by crystallization from methanol: IR (Nujol) 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, 3 H, J = 6 Hz), 3.5 (s, 3 H), 3.95 (m, 1 H), 4.2–5.1 (m, 4 H); MS, *m/e* 413 (M^+), 383, 354, 296, 286, 242, 226, 184, 168, 99.

Methyl 2-Iodo-3-amino-2,3,6-trideoxy-α-L-galactopyranoside Hydrochloride (8). A solution of **7** (4.55 g, 11 mmol) in methanol (40 mL) containing 2 N HCl (4 mL) was stirred for 24 h at room temperature. After removal of the solvent, the residue was crystallized from methanol/Et_2O (50:50) to give 3.4 g (95%) of **8** as a white solid: mp 210–213 °C dec; ^{1}H NMR (CD_3OD) δ 1.2 (d, 3 H, J = 6 Hz), 3.35 (s, 3 H), 3.7–4.5 (m, 4 H), 4.75 (bs, 4 H, OH, NH_3^+), 4.8 (bs, 1 H); $[\alpha]_D$ −104° (*c* 0.15, MeOH); MS, *m/e* 256 (M^+ − OCH_3), 171, 129, 99.

Methyl 3-Amino-2,3,6-trideoxy-α-L-lyxopyranoside Hydrochloride (Methyl α-L-Daunosaminide Hydrochloride) (1). To a solution of **8** (2.6 g, 8 mmol) and azobis(isobutironitrile) (1.32 g, 8 mmol) in benzene (25 mL) and methanol (5 mL) was added dropwise tri-*n*-butyltin hydride (4.6 g, 16 mmol), and the mixture was refluxed for 5 h. The solvents were removed under vacuum, and the residue was chromatographed on a silica gel column (ethyl acetate:methanol 8:2) to give 1.38 g (88%) of **1** as a white solid: mp 185–188 °C (lit.[1b] 188–190 °C); ^{1}H NMR (pyridine-d_5) δ 1.35 (d, 3 H, J = 6 Hz), 2.2–2.5 (m, 2 H), 3.25 (s, 3 H), 3.9 (q, 1 H), 4.2 (dt, 1 H), 4.5 (bs, 1 H), 4.8 (bs, 1 H), 8.3 (bs, 4 H, OH, NH_3^+); $[\alpha]_D$ −138° (*c* 0.2, MeOH) (lit.[1b] −140° (*c* 1, MeOH)).

Methyl 4-*O*-Acetyl-3-acetamido-2,3,6-trideoxy-α-L-lyxopyranoside (9). Acetic anhydride (2.5 mL) was added at room temperature to a solution of **1** (1.38 g, 7 mmol) in pyridine (5 mL), and the solution was stirred for 48 h. Pyridine and excess acetic anhydride were removed by azeotropic distillation with toluene under reduced pressure, and the residue was purified by silica gel chromatography (ethyl acetate:cyclohexane 7:3) to give 1.37 g (80%) of **9** as a white solid: mp 186–188 °C (lit.[1b] 188–189 °C); IR (Nujol) 3420, 1740, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1 (d, 3 H, J = 6 Hz), 1.75 (m, 2 H), 1.9 (s, 3 H), 2.15 (s, 3 H), 3.3 (s, 3 H), 4.0 (dq, 1 H), 4.3–4.6 (m, 1 H), 4.75 (m, 1 H), 5.0 (m, 1 H), 5.9 (d, NH, J = 7 Hz); MS, m/e 214 (M^+ − OCH_3), 185, 153, 142, 138, 101, 100; $[\alpha]_D$ −245° (*c* 1, MeOH) (lit.[1b] −248° (*c* 1, MeOH)).

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Registry No. 1, 32385-06-1; **2**, 40246-38-6; **3**, 40246-39-7; **4**, 63902-57-8; **5**, 91463-72-8; **6**, 88761-78-8; **7**, 88824-29-7; **8**, 91366-56-2; **9**, 18981-63-0.