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Note

Short stereoselective synthesis of L-nogalose

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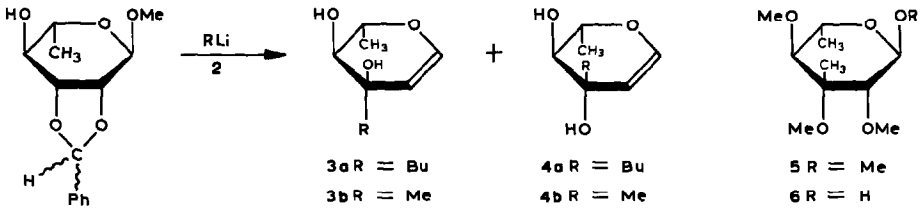
The remarkable reaction of the 2,3-benzylidene acetal (**1**) of methyl α-L-rhamnopyranoside with alkyllithium reagents [**2**, R = Bu (ref. 1), R = Me (ref.2)] provides easy access to a mixture[2,3] of the C-3-substituted glycals **3** and **4**. It occurred to us that this fragmentation–addition reaction might serve as a convenient entry to the synthesis of branched-chain sugars[4]. (For the use of glycal **4** in trisaccharide synthesis, see ref. 5). We now report that this strategy has been applied to the efficient synthesis (9 steps total, from L-rhamnose) of methyl α-L-nogalopyranoside (**5**). (For previous syntheses, see ref. 6). This constitutes a formal, total synthesis of L-nogalose[7] (**6**), the sugar component of the antitumor antibiotic nogalamycin[8].



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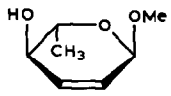

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The 2,3-benzylidene acetal (**1**) of methyl α-L-rhamnopyranoside was prepared in two steps[1] (96% yield) and treated with methyllithium according to the procedure of Jung and Klemer[2]. Chromatography of the product mixture[3] gave two fractions.

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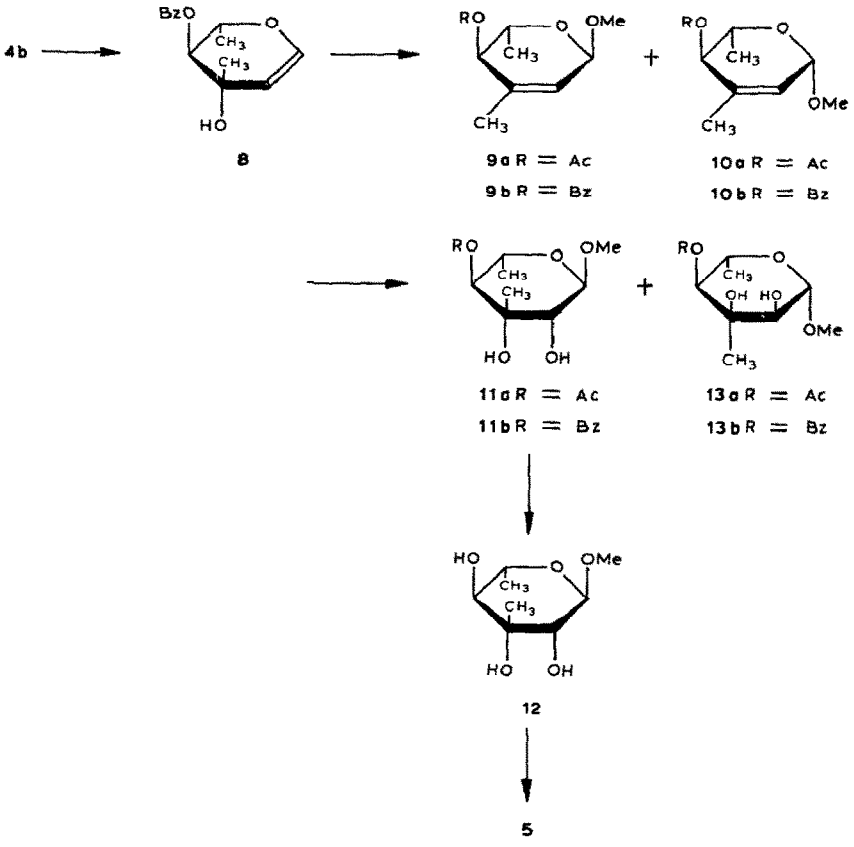
Analysis of a n.m.r. spectrum of the first fraction suggested that it contained glycal **3b** and methyl 2,3,6-trideoxy α-L-*erythro*-hex-2-enopyranoside (**7**)*. The second fraction consisted of glycal **4b**; this crystalline product was recovered in 61% yield from rhamnopyranoside **1**.

Glycal **4b** was converted into a mixture of glycosides **9a** and **10a** in the ratio of ~1:1 by treatment with acetic anhydride–4-(dimethylamino)pyridine, followed by quenching with anhydrous methanol. Equilibration of this mixture (*p*-toluenesulfonic acid–methanol) gave a new mixture enriched in the α anomer (**9a:10a** = 84:16; 72% from glycal **4b**).

Osmylation with osmium tetraoxide resulted in recovery of only 37% of diol **11a**; the low yield of this reaction was attributed to the water solubility of the products. Therefore, glycal **4b** was first converted into the 4-*O*-benzoyl derivative **8** in 77% yield by treatment with benzoyl chloride and an excess of potassium carbonate in acetonitrile. [Benzoylation with benzoyl chloride in pyridine or in pyridine



* Jung and Klemer[2] did not report the formation of hexenopyranoside **7** from the reaction of **1** with methyllithium; however, they did obtain this compound from the reaction of **1** with LDA. The n.m.r. spectra of **3b** and **4b** are recorded in ref. 3; the n.m.r. spectrum of **7** is recorded in ref. 2.

with added 4-(dimethylamino)pyridine did not proceed to completion even with a large excess of reagent and extended reaction-times.]

Treatment of glycal **8** with acetic anhydride and 4-(dimethylamino)pyridine followed by quenching of the reaction with anhydrous methanol gave glycosides **9b** and **10b** in the ratio of ~1:1. Equilibration of the product mixture with *p*-toluenesulfonic acid in methanol allowed recovery of the glycosides, now enriched in the α-glycoside (**9b:10b** = 86:14; ratio determined by analysis of the ^{1}H-n.m.r. spectrum), in a yield of 82% from glycal **8**. (Physical data for **9b** in the D series are reported in ref. 9.)

The conversions of glycals **4b** and **8** into glycosides **9a,10a** and **9b,10b**, respectively, appear to be the first examples of Ferrier-type rearrangements[10] of C-3-branched glycal esters. These are presumably expecially facile because of the added stability of the carbonium ion intermediate. (This reaction may be compared with the rearrangement of the unbranched rhamnal diacetate, which apparently required Lewis acid conditions[10b].)

Because the mixture of **9b** and **10b** exhibited a single spot on t.l.c. with 3:1 hexane–ethyl acetate, no attempt was made to separate the anomers. Osmylation of this 86:14 mixture resulted in quantitative conversion into a mixture of two *cis*-diol products; these were easily separated by flash chromatography. On the basis of its n.m.r. spectrum, the major component (80% from the mixture of **9b** and **10b**) was determined to be the desired intermediate **11b**. Debenzoylation of diol **11b** with a 0.1M solution of sodium methoxide in methanol gave crystalline methyl α-L-evalopyranoside (**12**) in 94% yield. [The osmylation of D-**9b** and debenzoylation of D-**11b** to give methyl α-D-evaloside (D-**12**), and complete physical data for D-**11b**, are given in ref. 11.]

Treatment of triol **12** with methyl iodide and sodium hydride in dimethyl sulfoxide[6b] afforded methyl α-L-nogalopyranoside (**5**) in 64% yield. This material was identical in all respects to a sample obtained by treating L-nogalose with 5% HCl in methanol[7]. A mixed melting point of material composed of synthetic material and material derived from natural nogalose was undepressed.

The minor product from the osmylation of **9b,10b** was tentatively identified as pyranoside **13b** on the basis of the following argument. Osmylation of D-**9b** is reported[11] to give only D-**11b**, as expected. Therefore, the minor product is presumably derived from **10b**, the minor component in the starting material. Treatment of the major osmylation product with 5% HCl in methanol converted it into a mixture of anomers, neither of which was the minor product; consequently, the minor diol is not the anomer of **11b** and must therefore be stereoisomeric to **11b** at C-2 and C-3. The n.m.r. data for the minor osmylation product are consistent with those expected for structure **13b**.

The 9-step synthesis of methyl α-L-nogalopyranoside proceeds in an overall yield of 21% from rhamnose and requires two chromatographic separations.

EXPERIMENTAL

General. — Solutions were evaporated under diminished pressure and extracts were dried (Na_2SO_4). Melting points were taken on a Thomas–Hoover apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter was used for measurement of specific rotations. Packing material for column chromatography was Merck silica gel 60. Infrared spectra were recorded with a Perkin–Elmer 681 spectrophotometer. ^{1}H-n.m.r. spectra were recorded with a Bruker 250 or Bruker 400 spectrometer. Chemical shifts are reported, relative to tetramethylsilane, in parts per million. High-resolution mass spectra were recorded with a Kratos MS-80 spectrometer under either e.i. or c.i. conditions (as indicated).

Methyl 2,3-O-benzylidene-6-deoxy-α-L-mannopyranoside (**1**). — The procedure of Clode *et al.*[1], applied to α-L-rhamnose (10 g, 61 mmol) afforded crude methyl α-L-rhamnopyranoside (12 g). A sample (1.00 g) of this noncrystalline material was treated according to the literature procedure for benzylidenation. Chromatography of the crude acetal on silica gel with 2:1 hexane–ethyl acetate afforded 1.31 g of acetal **1** as a syrup (96% form α-L-rhamnose).

*1,5-Anhydro-1,2,6-trideoxy-3-C-methyl-*L*-ribo-hex-1-enitol* (**4b**). — Benzylidene acetal **1** was treated with methyllithium (15.0 mL, 22.6 mmol) according to the procedure of Jung and Klemer[2]. After the reaction had been quenched with 10% ammonium chloride (25 mL) and the THF removed on a rotary evaporator, the remaining aqueous mixture was continuously extracted for 48 h with dichloromethane. The extract was dried, filtered, and evaporated, to yield 940 mg of a yellow oil which was subjected to column chromatography (3:2 and then 2:3 hexane–ethyl acetate). The first fraction (113 mg) contained two compounds which were assigned structures **3b** and **7** on the basis of the ^{1}H-n.m.r. data[1]. The second fraction contained glycal **4b** (330 mg, 61%). As glycal **3b** could not be separated from hexenopyranoside **7**, only glycal **4b** was used in the next reaction.

Compound **4b** had m.p. 101–103° (from ether–pet. ether), $[\alpha]_D^{23}$ −60° ($CHCl_3$); lit.[2] m.p. 104–106°, $[\alpha]_D^{20}$ −61.9° (in THF).

*Methyl 4-O-acetyl-2,3,6-trideoxy-3-C-methyl-α-*L*-erythro-hex-2-enopyranoside and its β anomer* (**9a** *and* **10a**). — To a solution of glycal **4b** (598 mg, 4.15 mmol) in acetic anhydride (4 mL) was added a solution of 4-(dimethylamino)pyridine (760 mg, 6.23 mmol) in acetic anhydride (3 mL). The mixture was stirred under nitrogen for 24 h at room temperature, cooled to 0°, and methanol (10 mL) added. Stirring was continued for an additional 4 h at room temperature. After removal of methanol by rotary evaporation, the residue was dissolved in dichloromethane and washed with water. After back extraction, the extracts were combined, successively washed with 5% HCl and saturated $NaHCO_3$, dried, filtered, and evaporated, to yield 705 mg of a yellow oil, apparently a mixture of α and β anomers **9a** and **10a** (~1:1, as indicated by the ^{1}H-n.m.r. spectrum).

Equilibration of this material to a mixture enriched in the α-anomer (84:16) was accomplished by treatment with methanol (15 mL) and a catalytic amount of

p-toluenesulfonic acid. The resulting mixture was stirred under reflux for 2 h. After removal of methanol by rotary evaporation, the residue was dissolved in dichloromethane. The solution was washed twice with saturated $NaHCO_3$, and dried, filtered, and evaporated. On purification by column chromatography (5:1 hexane–ethyl acetate), the residue afforded a pale yellow oil (598 mg, 72% from glycal **4b**); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 5.64 (m, 0.16 H, H-2 in **10a**), 5.56 (m, 0.84 H, H-2 in **9a**), 5.19 (bd, 0.84 H, $J_{4,5}$ 9.1 Hz, H-4 in **9a**), 5.08 (bd, 0.16 H, $J_{4,5}$ 6 Hz, H-4 in **10a**), 5.00 (m, 0.16 H, H-1 in **10a**), 4.82 (bs, 0.84 H, H-1 in **9a**), 3.93 (dq, 0.84 H, $J_{5,4}$ 9.1, $J_{5,6}$ 6.3 Hz, H-5 in **9a**), 3.88 (m, 0.16 H, H-5 in **10a**), 3.44 (s, 0.48 H, OMe in **10a**), 3.41 (s, 2.52 H, OMe in **9a**), 2.11 (s, 2.52 H, OAc), 1.72 (m, 0.48 H, Me-3 in **10a**), 1.67 (m, 2.52 H, Me-3 in **9a**), 1.30 (d, 0.48 H, $J_{6,5}$ 6.3 Hz, H-6 in **10a**), and 1.20 (d, 2.52 H, $J_{6,5}$ 6.3 Hz, H-6 in **9a**); ν_{max}^{neat} 2900, 1740, 1660, 1435, and 1360 cm^{-1}.

Methyl 4-O-acetyl-6-deoxy-3-C-methyl-α-L-mannopyranoside (**11a**) *and* (**13a**). — Alkene **9a** (100 mg, 0.5 mmol) was hydroxylated with osmium tetraoxide according to the procedure of Valente *et al.*[11]. After cleavage of the osmic ester by addition of sodium hydrogensulfite, the mixture was partitioned between water and dichloromethane. The organic layer was washed several times with 5% HCl, dried, filtered, and evaporated, to a syrup (73.8 mg) which was subjected to column chromatography (7:5 hexane–ethyl acetate followed by ethyl acetate). Diol **11a** was eluted first, followed by diol **13a**.

Compound **11a** weighed 59.7 mg (44% from **9a**); ^{1}H-n.m.r. (400 MHz, $CHCl_3$): δ 4.81 (d, $J_{4,5}$ 9.8 Hz, H-4), 4.73 (d, $J_{1,2}$ 1.2 Hz, H-1), 3.76 (dq, $J_{5,4}$ 9.8, $J_{5,6}$ 6.3 Hz, H-5), 3.65 and 2.38 (both bs, 1 H, exchanged with D_2O), 3.58 (d, $J_{2,1}$ 1.2 Hz, H-2), 3.38 (s, OMe), 2.14 (s, OAc), 1.30 (s, Me-3), and 1.21 (d, $J_{6,5}$ 6.3 Hz, H-6); ν_{max}^{neat} 3500 (b), 2900, 1750, and 1440 cm^{-1}.

Compound **13a** weighed 6.9 mg (3% from **10a**); ^{1}H-n.m.r. (400 MHz, $CHCl_3$): δ 4.64 (d, $J_{4,5}$ 9.7 Hz, H-4), 4.48 (d, $J_{1,2}$ 7.8 Hz, H-1), 3.93 (dq, $J_{5,4}$ 9.7, $J_{5,6}$ 6.3 Hz, H-5), 3.55 (s, OMe), 3.27 (d, $J_{2,1}$ 7.8 Hz, H-2), 2.49 and 2.24 (both bs, 1 H, exchanged with D_2O), 2.17 (s, OAc), 1.26 (s, Me-3), and 1.18 (d, $J_{6,5}$ 6.3 Hz, H-6); ν_{max}^{neat} 3500 (b), 2900, 1750, and 1440 cm^{-1}.

1,5-Anhydro-4-O-benzoyl-1,2,6-trideoxy-3-C-methyl-L-ribo-*hex-1-enitol* (**8**). — To a stirred solution of diol **4b** (20 mg, 0.14 mmol) in acetonitrile (15 mL) was added an excess (20 equiv.) of K_2CO_3. The resulting mixture was cooled (Dry Ice) and benzoyl chloride (0.16 mL, 1.4 mmol) was added dropwise under nitrogen. After the addition was complete, the mixture was allowed to warm to room temperature and then stirred for 24 h at 60°. The K_2CO_3 was removed by filtration and washed several times with dichloromethane. After evaporation of the combined organic solution, the yellow residue was purified by column chromatography (4:1 hexane–ethyl acetate) to afford monobenzoate **8** (26.6 mg, 77%) as a colorless oil. A pure sample was obtained by distillation (kugelrohr 145°/0.45 mmHg); m.p. 65–67°, $[\alpha]_D^{13}$ −116.3°; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.15–8.0 and 7.7–7.3 (m, 5 H), 6.26 (d, $J_{1,2}$ 6 Hz, H-1), 5.25 (d, $J_{4,5}$ 10 Hz, H-4), 4.83 (d, $J_{2,1}$ 6 Hz, H-2), 4.12 (dq, $J_{5,4}$ 10, $J_{5,6}$ 6.3 Hz, H-5), 3.13 (bs, 1 H, exchanged with D_2O), 1.43 (s, Me-3), and

1.33 (d, $J_{6,5}$ 6.3 Hz, H-6); $\nu_{max}^{CHCl_3}$ 3500 (b), 2980, 1720, 1645, 1450, and 1265 cm^{-1}; e.i.-m.s. Calc. for $C_{14}H_{16}O_4$: 248.1048, Found: 248.1048.

*Methyl 4-O-benzoyl-2,3,6-trideoxy-3-C-methyl-α-*D*-erythro-hex-2-enopyranoside and its β anomer* **9b** *and* **10b**). — To a solution of glycal **8** (154 mg, 0.62 mmol) in acetic anhydride (5 mL) was added a solution of 4-(dimethylamino)pyridine (151.4 mg, 1.24 mmol) in acetic anhydride (5 mL). The mixture was stirred under nitrogen for 5 h at 60°, cooled to 0°, methanol (5 mL) was added, and stirring was continued for an additional 8 h at room temperature. After removal of methanol by rotary evaporation, the residue was dissolved in dichloromethane and the solution washed with water. After back extraction, the extracts were combined, successively washed with 5% HCl and saturated $NaHCO_3$, dried, filtered, and evaporated, to yield 167 mg of a yellow oil, apparently a mixture of the α- and β anomers (14:11) as judged by the ^{1}H-n.m.r. spectrum. Equilibration of this material to a mixture enriched in the α anomer (86:14) was accomplished by treatment with methanol (7 mL) and a catalytic amount of *p*-toluenesulfonic acid. The resulting mixture was stirred under reflux for 2 h. After removal of methanol by rotary evaporation, the residue was dissolved in dichloromethane. The solution was washed twice with saturated $NaHCO_3$, dried, filtered, and evaporated. The residue, after purification by column chromatography (10:1 hexane–ethyl acetate) afforded a colorless oil (133 mg, 82% from glycal **8**): kugelrohr 175°/60 0.45 mmHg; $[\alpha]_D^{13}$ −131° ($CHCl_3$); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.15–8.0 and 7.7–7.3 (m, 5 H), 5.68 (m, 0.14 H, H-2 in **10b**), 5.62 (m, 0.86 H, H-2 in **9b**), 5.48 (bd, 0.86 H, $J_{4,5}$ 9.3 Hz, H-4 in **9b**), 5.42 (bd, 0.14 H, $J_{4,5}$ 6 Hz, H-4 in **10b**), 5.08 (m, 0.14 H, H-1 in **10b**), 4.88 (bs, 0.86 H, H-1 in **9b**), 4.11 (dq, 0.86 H, $J_{5,4}$ 9.3, $J_{5,6}$ 6.3 Hz, H-5 in **9b**), 3.99 (m, 0.14 H, H-5 in **10b**), 3.48 (s, 0.42 H, OMe in **10b**), 3.46 (s, 2.58 H, OMe in **9b**), 1.76 (m, 0.42 H, Me-3 in **10b**), 1.70 (m, 2.58 H, Me-3 in **9b**), 1.36 (d, 0.42 H, $J_{6,5}$ 6.3 Hz, H-6 in **10b**), and 1.26 (d, 2.58 H, $J_{6,5}$ 6.3 Hz, H-6 in **9b**); ν_{max}^{neat} 2940, 1720, 1595, 1445, and 1260 cm^{-1}; c.i-m.s. (isobutane); Calc. for ($C_{15}H_{18}O_4$+H−CH_3OH): 231.1021. Found 231.1037.

*Methyl 4-O-benzoyl-6-deoxy-3-C-methyl-α-*L*-mannopyranoside* (**11b**) *and* (**13b**). — A 86:14 mixture of alkenes **9b** and **10b** (133 mg, 0.51 mmol) was hydroxylated with osmium tetraoxide according to the procedure of Valente *et al.*[11]. After cleavage of the osmic ester by addition of sodium hydrogensulfite, the mixture was partitioned between water and dichloromethane. The organic layer was washed several times with 5% HCl, dried, filtered, and evaporated, to yield a syrup (150 mg) which was subjected to chromatography (chromatatron, silica, hexane–ethyl acetate: 2:1 followed by 1:1). Diol **11b** was eluted first, followed by diol **13b**.

Compound **11b** weighed 121.5 mg (95% from **9b**); kugelrohr 123°/0.65 mmHg; $[\alpha]_D^{13}$ −111° ($CHCl_3$); ^{1}H-n.m.r. (250 MHz, $CHCl_3$): δ 8.15–8.0 and 7.7–7.3 (m, 5 H), 5.08 (d, $J_{4,5}$ 9.8 Hz, H-4), 4.79 (d, $J_{1,2}$ 1.3 Hz, H-1), 3.94 (dq, $J_{5,4}$ 9.8, $J_{5,6}$ 6.3 Hz, H-5), 3.81 (bs, 2 H, exchanged with D_2O), 3.64 (d, $J_{2,1}$ 1.3 Hz, H-2), 3.41 (s, OMe), 1.41 (s, Me-3), and 1.27 (d, $J_{6,5}$ 6.3 Hz, H-6); $\nu_{max}^{CHCl_3}$ 3500 (b), 2990, 2910, 1720, 1600, and 1450 cm^{-1}; c.i.-m.s. (isobutane): Calc. for $C_{15}H_{20}O_6$+H:

297.1338. Found 297.1438.

Compound **13b** weighed 21 mg (99% from **10b**); ^{1}H-n.m.r. (250 MHz, $CHCl_3$): δ 8.15–8.0 and 7.7–7.3 (m, 5 H), 4.91 (d, $J_{4,5}$ 9.7 Hz, H-4), 4.55 (d, $J_{1,2}$ 7.8 Hz, H-1), 4.10 (m, H-5), 3.58 (s, OMe), 3.34 (d, $J_{2,1}$ 7.8 Hz, H-2), 2.61 and 2.32 (both bs, 1 H, exchanged with D_2O), 1.31 (s, Me-3), and 1.23 (d, $J_{6,5}$ 6.3 Hz, H-6); $\nu_{max}^{CHCl_3}$ 3500 (b), 2990, 2910, 1720, 1600, and 1450 cm^{-1}.

*Methyl 6-deoxy-3-*C*-methyl-*α*-*L*-mannopyranoside* (**12**). — A solution of diol **11b** (82.8 mg, 0.28 mmol) in 0.1M methanolic sodium methoxide (7 mL) was stirred for 4 h at room temperature under nitrogen and then made neutral with Amberlite IR-120 (H^+) resin, which was removed by filtration. Evaporation of the solution, followed by removal of methyl benzoate under high vacuum, afforded triol **12** (50.6 mg, 94%) as a white solid; m.p. 129–130° (from ether–hexane), $[\alpha]_D^{13}$ −81.5° ($CHCl_3$); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 4.69 (bs, H-1), 3.66–3.51 (m, 3 H), 3.38 (s, OMe), 2.94 (bs, 2 H, exchanged with D_2O), 2.44 (bs, 1 H, exchanged with D_2O), 1.33 (s, Me-3), and 1.31 (d, $J_{6,5}$ 6.2 Hz, H-6); $\nu_{max}^{CHCl_3}$ 3500(b), 3000, 2940, 1130, and 1075 cm^{-1}; c.i.$^+$-m.s., (NH_3): Calc. for $C_8H_{16}O_5+NH_4$): 210.1441. Found: 210.1341.

*Methyl 6-deoxy-3-*C*-methyl-2,3,4-tri-*O*-methyl-*α*-*L*-mannopyranoside (methyl *α*-*L*-nogalopyranoside)* (**5**). — Treatment of a 27.8-mg sample of triol **12** in Me_2SO with iodomethane according to Giuliano[6c] gave a yellow oil, which, when placed on a column of silica (3:1 hexane–ethyl acetate), afforded pyranoside **5** (21.1 mg, 64%). A pure sample was obtained by kugelrohr distillation: at 67°/0.5 mmHg; m.p. 41–43, $[\alpha]_D^{13}$ −52.7° ($CHCl_3$); lit.[7] m.p. 41–43°, $[\alpha]_D^{25}$ −48.4° (methanol); ^{1}H-n.m.r. (250 MHz, $CDCl_3$)[6b].

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