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SYNTHESIS OF MYCAROSE AND EPI-AXENOSE FROM NON-CARBOHYDRATE PRECURSORS*

WILLIAM R. ROUSH** AND SUSANNAH M. HAGADORN
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (U.S.A.)
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ABSTRACT

A six-step synthesis of racemic mycarose from allylacetylene is described. Key transformations include the *threo*-selective epoxidation of (*E*)-4-methyl-1,4-heptadien-6-ol and the α-opening of *xylo*-4,5-epoxy-4-methylhept-1-en-6-ol (**7**), which was accomplished *via* a neighboring group-assisted reaction of *xylo*-4,5-epoxy-4-methyl-6-(*N*-phenylcarbamoyloxy)hept-1-ene (**12**). The latter conversion proceeded with lower selectivity (3:1) than observed with disubstituted epoxyurethanes because of the greater tendency of trisubstituted epoxides to undergo substitutions with S_N1 character at the tertiary center. Methanolysis of *ribo*-4-methylhept-1-ene-4,5,6-triol 5,6-carbonate, obtained from **12** in up to 61% yield, afforded *ribo*-4-methylhept-1-ene-4,5,6-triol, which was converted into mycarose by ozonolysis. Similarly, ozonolysis of *lyxo*-4-methylhept-1-ene-4,5,6-triol, which was prepared (64%) by hydrolysis of **7**, afforded racemic 3-epi-axenose.

INTRODUCTION

The synthesis of carbohydrates and polyhydroxylated compounds from non-carbohydrate precursors is a topic of considerable current interest[1,2]. Among other reasons, simple monosaccharides are ideal targets for demonstrating new strategies for control of stereochemistry in acyclic systems. We recently described[2] methodology for selective α-opening of epoxy alcohols (**1**) via neighboring group-assisted reactions of the derived phenylurethanes (*e.g.*, **2**→**3**). Complementary regioselectivity was accomplished by hydrolysis of the epoxyalcohol substrates with aqueous acid (*e.g.*, **1**→**4**). By use of these procedures, short, highly stereoselective syntheses were accomplished of all four isomers of 2,6-dideoxyhexose (the *arabino, lyxo,* and *ribo* isomers were prepared enantioselectively)[3]. We now describe extensions of this methodology towards the synthesis of 2,6-dideoxy-3-*C*-methyl-*ribo*-hexose (**5**, mycarose)[4] and 2,6-dideoxy-3-*C*-methyl-*lyxo*-hexose (**6**, 3-epi-axenose)[5] via the epoxyalcohol **7**.

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**Roger and Georges Firmenich Career Development Associate Professor of Natural Products Chemistry, 1981–1984; Fellow of the Alfred P. Sloan Foundation, 1982–84.

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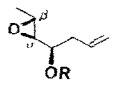

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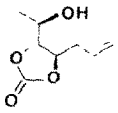

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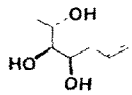

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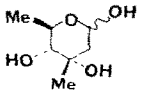

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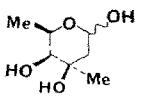

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RESULTS AND DISCUSSION

The key intermediate **7** was synthesized starting from allylacetylene (**8**). Thus, treatment of **8** with 2 equiv. of trimethylaluminum in dichloromethane in the presence of 0.25 equiv. of bis(cyclopentadienyl)zirconium dichloride (0°→25°, 24 h) followed by 3 equiv. of acetaldehyde afforded[6] the allylic alcohol **9**, which was epoxidized[7] by using titanium(IV) isopropoxide and *tert*-butylhydroperoxide in dichloromethane at −20°. The latter procedure is highly *threo*-selective (>19:1) and afforded **7** in good yield (84% from **8**).

Completion of a synthesis of mycarose from **7** required that a selective α-opening of the epoxide be accomplished, whereas a β-opening of **7** would lead to the *lyxo*-triol precursor to **6**. The latter conversion was readily accomplished by exposure of **7** to 0.1M sulfuric acid in aqueous tetrahydrofuran (1:4) at 45° for 38 h. In this manner, 64% of the *lyxo*-triol **11** was obtained uncontaminated by the *ribo*-isomer **10**, and also 11% of *threo*-4-methyl-1,3-heptadiene-5,6-diol. The conversion of **7** into **10**, however, was less straightforward. The phenylurethane **12** was prepared (72%) from **7** by the usual procedure (phenyl isocyanate, pyridine, 25°). Treatment of **12** with various Lewis acids under aprotic conditions (see Table I) afforded a mixture of (at least) three carbonates **13–15** which were not isolated in preliminary experiments. Such mixtures were hydrolyzed (methanolic 0.2M sodium methoxide, 23–60°) to give a mixture of triols **10** and **11**, the ratio of which was

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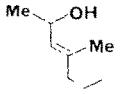

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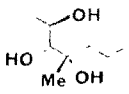

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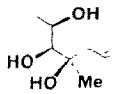

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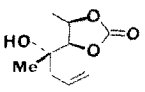
12 R = CONHPh



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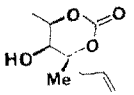

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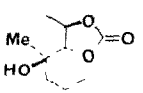

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TABLE I

REACTIONS OF URETHANE **12** WITH LEWIS ACIDS

Entry	*Conditions*[a]	*Products*[b,c] *(%)*	
		10 + **11** (ratio)	**16**[d]
1	Diethylaluminum chloride (3–6 equiv.), dimethoxyethane, 20 h	53 (3:1)	—
2	Diethylaluminum chloride (3 equiv.), ether, 20 h	62 (2:1)	—
3	Diethylaluminum chloride (4.5 equiv.), tetrahydrofuran, 24 h[e]	23 (1:10)	—
4	Diethylaluminum chloride (3 equiv.), toluene, 8 h	33 (1:1.5)	—
5	Diethylaluminum chloride (3 equiv.), dichloromethane, 4 h	—	*f*
6	Boron trifluoride etherate (3 equiv.), ether, 5 h	62 (1:2)	—
7	Boron trifluoride etherate (3 equiv.), dichloromethane, 2 h	52 (1:5)	—
8	Stannic chloride (3 equiv.), dichloromethane, 2 h	35 (1:2)	35
9	Trimethylaluminum (1.2 equiv.), ether, 16 h[g]	35 (1:1)	—

[a]With the exception of entry 3, all epoxide openings were performed at −20°. Work-up involved mild treatment with acid to hydrolyze the intermediate imino carbonates. The mixture of carbonates so produced was then treated with sodium methoxide in methanol, as described in the Experimental. [b]Yields are for isolated products. [c]The ratio was determined by n.m.r. spectroscopy before chromatography of the mixture. [d]Compound **16** is *threo*-4-methyl-2-(*N*-phenylcarbamoyloxy)-4,6-heptadien-3-ol, produced by an elimination reaction. [e]Warmed from −20° to 25°. [f]Diene **16** was obtained in near quantitative yield. [g]Urethane **12** (59%) was recovered before the NaOMe step.

determined by high-field n.m.r. spectroscopy. The greatest selectivity for α-opening was obtained by using diethylaluminum chloride in dimethoxyethane at −20° in the epoxide-opening step, leading to a 3:1 mixture of **10** and **11** after deacylation. Under all other conditions examined, greater amounts of intramolecular addition of the urethane carbonyl group to the β-position of **12**, leading ultimately to **11** via γ-carbonate **14** and its acyl-transfer isomer **15**, or elimination to diene **16**, were observed. The magnitude of the problem of intramolecular β-epoxide opening, which was encountered to only a limited extent in studies of disubstituted epoxyurethanes[2], reflects the greater tendency of trisubstituted epoxides to undergo substitutions with S_N1 character at the tertiary center.

For preparative scale work, it proved most convenient to purify **13** (yield up to 61%) from the reaction specified in entry 1 of Table I (mixtures of triols **10** and **11** could be fractionated only with difficulty). Transesterification of **13**, according to the procedure described above, provided 90–95% of triol **10**, ozonolysis of which (ozone–methanol, −20°; then dimethyl sulfide at 25°) gave 92% of racemic mycarose (**5**). Similarly, 3-epi-axenose was prepared (89%) from *lyxo*-triol **11**. The structures of these sugars were confirmed by conversion into the corresponding methyl pyranosides (methanol, acetyl chloride, 23°) (an α,β-mixture was obtained from which the α anomer was separated by chromatography). The spectroscopic properties of methyl α-mycaroside were identical to literature data[4b], and those of methyl α-3-epi-axenopyranoside were identical to those of an authentic sample[5].

EXPERIMENTAL

General. — ^{1}H-N.m.r. spectra were recorded with a Bruker 250-MHz instrument for solutions in $CDCl_3$ (internal $CHCl_3$, δ 7.24). I.r. spectra were recorded with a Perkin–Elmer Model 283B spectrophotometer and were calibrated with the 1601 cm^{-1} absorption of polystyrene. Mass spectra were measured at 70 eV on a Finnegan MAT 8200 instrument. Elemental analyses were performed by Robertson Laboratories (Florham Park, NJ). Melting points were recorded on a Fisher–Johns hot-stage melting-point apparatus and are uncorrected.

All reactions were conducted in oven-dried (120°) glassware under dry nitrogen. All solvents were purified before use according to the procedures previously described[2]. Preparative t.l.c. was performed on 0.5- and 2-mm layers of silica gel (Analtech). Column chromatography was performed on silica gel (activity I, Woelm). All chromatography solvents were distilled prior to use.

xylo-*4,5-Epoxy-4-methylhept-1-en-6-ol* (**7**). — To a stirred solution of bis-cyclopentadienylzirconium dichloride (1.2 g, 4.8 mmol) and trimethylaluminum (34 mmol, 2M in toluene) in CH_2Cl_2 (50 mL) at −15° was added a solution of allylacetylene (1.0 g, 15 mmol) in CH_2Cl_2 (5 mL). The solution was stirred at 23° under argon for 24 h and then cooled to −12°. A solution of freshly distilled acetaldehyde (2.4 g, 53 mmol) in CH_2Cl_2 (8 mL) was added dropwise. The resulting straw-colored mixture was stirred at 23° for 3 h, then cooled to −10°, and quenched with saturated aqueous K_2CO_3 (5 mL, exothermic reaction). This mixture was stirred for 2 h until the evolution of gas ceased. The resulting fine white suspension was filtered through a Celite pad, and the solid residue was washed with CH_2Cl_2 (total, 150 mL). The combined filtrate and washings were extracted with saturated aqueous NaCl and dried ($MgSO_4$). The allylic alcohol **9** is somewhat volatile, and consequently the crude product was used directly in the next step. Pure **9** had ν_{max} 3350, 3080, 1640, and 1050 cm^{-1}. ^{1}H-N.m.r. data: δ 1.21 (d, 3 H, $J_{6,7}$ 6 Hz, H-7), 1.64 (d, 3 H, $J_{8,5}$ 1 Hz, H-8), 2.69 (d, 2 H, $J_{2,3}$ 6 Hz, H-3), 4.55 (m, 1 H, H-6), 5.03 (m, 2 H, H-1), 5.22 (m, 1 H, H-5), 5.75 (m, 1 H, H-2).

Anal. Calc. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.14; H, 11.47.

Methylene chloride (~30 mL) was distilled from a solution of crude **9**. The residue was cooled to −20° and treated with $Ti(OiPr)_4$ (3.4 g, 12 mmol) and *tert*-butyl hydroperoxide (15 mmol, 5.05M in CH_2Cl_2). The solution was stored at −20° for 20 h, and ether (80 mL) and saturated aqueous Na_2SO_4 (5 mL) were then added. The mixture was stirred vigorously at room temperature for 1 h, filtered through Celite, dried ($MgSO_4$), and concentrated *in vacuo* without heating. The resulting yellow oil (2.2 g) was distilled twice (b.p. 110–115°/30 mmHg) to give **7** (1.8 g, 84%), which was at least 95% isomerically pure; ν_{max} 3420, 3080, 1640, and 1060 cm^{-1}. ^{1}H-N.m.r. data: δ 1.22 (d, 3 H, $J_{1,2}$ 7 Hz, H-7), 1.28 (s, 3 H, H-8), 2.27 (m, 2 H, H-3), 2.63 (s, 1 H, OH), 2.75 (d, 1 H, $J_{2,3}$ 8 Hz, H-5), 3.65 (m, 1 H, H-6), 5.08 (m, 2 H, H-1), 5.73 (m, 1 H, H-2). Mass spectrum: *m/z* 123, 109.

Anal. Calc. for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.36; H, 10.04.

xylo-*4,5-Epoxy-4-methyl-6-(N-phenylcarbamoyloxy)hept-1-ene* (**12**). — A mixture of **7** (1.0 g, 7.0 mmol), phenyl isocyanate (5.0 g, 35 mmol), and pyridine (5 mL) in CH_2Cl_2 (50 mL) was stirred for 18 h at 23°. The solvent was then removed *in vacuo* and the residue treated with aqueous 10% acetone (50 mL) for 1.5 h. The resulting white solid was collected and triturated with CH_2Cl_2. Evaporation of the solvents gave a yellow oil which was purified by flash column chromatography (9:1 hexane–ether) on silica gel (50 g) to give isomerically pure **12** (1.3 g, 72%). On a smaller scale (150 mg of **7**), **12** containing 5% of *erythro*-epoxide isomer was obtained in 95% yield; $\nu_{max}^{CH_2Cl_2}$ 3420, 1740, 1510, and 1215 cm^{-1}. ^{1}H-N.m.r. data: δ 1.32 (d, 3 H, $J_{6,7}$ 7 Hz, H-7), 1.33 (s, 3 H, H-8), 2.30 (m, 2 H, H-3), 2.88 (d, 1 H, $J_{5,6}$ 8 Hz, H-5), 4.73 (m, 1 H, H-6), 5.11 (m, 2 H, H-1), 5.74 (m, 1 H, H-2), 6.79 (s, 1 H, NH), 7.0–7.4 (m, Ph). Mass spectrum: *m/z* 262 ($M^+ + 1$), 261 (M^+), 125.

Anal. Calc. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.34; N, 5.36. Found: C, 69.21; H, 7.66; N, 5.65.

lyxo-*4-Methylhept-1-ene-4,5,6-triol* (**11**). — Compound **7** (54 mg, 0.39 mmol) was treated for 38 h at 45° with tetrahydrofuran–0.1M H_2SO_4 (4:1, 5 mL). The mixture was filtered through Dowex 1-X8 (Na^+) resin and concentrated. The resulting yellow oil was purified by preparative t.l.c. (4:1 ether–hexane) to give **11** (39 mg, 64%); ν_{max} 3490, 3025, and 1040 cm^{-1}; and *threo*-4-methyl-1,3-heptadiene-5,6-diol (6 mg, 11%). ^{1}H-N.m.r. data: δ 1.24 (m, 6 H, H-7,8), 2.34 (m, 2 H, H-3), 2.9–3.2 (m, 4 H, H-5 and HO-2,3,4), 4.21 (q, 1 H, $J_{5,6} = J_{6,7} = 8$ Hz, H-6), 5.09 (m, 2 H, H-7), 5.78 (m, 1 H, H-6). Mass spectrum: *m/z* 125, 119.

Anal. Calc. for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.64; H, 10.11.

ribo-*4-Methylhept-1-ene-4,5,6-triol 5,6-carbonate* (**13**). — A solution of **12** (148 mg, 0.57 mmol) in dimethoxyethane (17 mL) was treated with Et_2AlCl (3.2 equiv., M in hexane) at −50°. The mixture was stored at −20° and more Et_2AlCl (2.5 equiv.) was added after 4 h. After a total of 18 h at −20°, 0.5M HCl (4 mL) was added dropwise, and the mixture was stirred at 23° for 2 h and then extracted with CH_2Cl_2 (4 × 10 mL). The combined extracts were washed with saturated aqueous NaCl–$NaHCO_3$, dried over K_2CO_3, filtered, and concentrated *in vacuo*. The crude product contained four carbonates: R_F 0.63 (ether), **13** and **15** (ν_{max} 1800 cm^{-1}; methanolysis of **15** afforded **11**); R_F 0.54 (minor), presumed to be *lyxo*-4-methylhept-1-ene-4,5,6-triol 4,5-carbonate (ν_{max} 1800 cm^{-1}); and R_F 0.35, identified as **14** (ν_{max} 1745 cm^{-1}) by hydrolysis to **11**. Chromatography (hexane–ether) of the crude product over silica gel (20 g) afforded a 20:1 mixture (65 mg, 61%) of **13** and **15**. In other runs, however, the ratio was ~10:1.

A mixture of **13** and **15** (167 mg) was chromatographed on a Harrison Research Chromatotron apparatus, using a rotor coated with a 2-mm layer of Merck PF 254 $CaSO_4 \cdot 0.5\ H_2O$ silica gel and eluted with methanol–benzene (1.5:98.5). After one recycle of mixed fractions, **13** (108 mg, 65%; ν_{max} 3450, 3060, 2980, and 1800 cm^{-1}), **15** (4 mg), and mixed fractions enriched in **15** (21 mg) were obtained. ^{1}H-N.m.r. data: δ 1.35 (s, 3 H, CMe), 1.60 (d, 3 H, H-7), 2.0 (s, 1 H, OH), 2.34 (m, 2 H, H-3), 4.75 (d, 1 H, H-5), 4.88 (m, 1 H, H-6), 5.20 (m, 2 H, H-1), 5.81 (m, 1 H, H-2).

Anal. Calc. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.90; H, 7.56.

ribo-*4-Methylhept-1-ene-4,5,6-triol* (**10**). — Carbonate **13** (178 mg, 1.05 mmol) was treated with methanolic 0.18M NaOMe (15 mL) at 23° or 60° for 13 h. The mixture was then filtered through Dowex 50W-X8 (H^+) resin, which had been pretreated with MeOH, and concentrated *in vacuo* to give **10** (137 mg, 90%); ν_{max} 3350, 3080, and 1040 cm^{-1}; which was pure enough for subsequent transformations. ^{1}H-N.m.r. data: δ 1.24 (s, 3 H, H-8), 1.28 (d, 3 H, $J_{6,7}$ 6.1 Hz, H-7), 2.08 (d, 1 H, $J_{5,OH}$ 5.5 Hz, HO-5), 2.32 (m, 2 H, H-3), 2.87 (s, 1 H, HO-4), 3.03 (d, 1 H, $J_{6,OH}$ 1.7 Hz, HO-6), 3.27 (dd, 1 H, $J_{5,6}$ 7.5, $J_{5,OH}$ 5.6 Hz, H-5), 3.93 (m, 1 H, H-6), 5.19 (m, 2 H, H-1), 5.94 (m, 1 H, H-2). Mass spectrum: *m/z* 119 ($M^+ - C_3H_5$), 85.

Anal. Calc. for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.96; H, 9.91.

2,6-Dideoxy-3-C-methyl-ribo-*hexose* (**5**, *mycarose*). — A solution of **10** (43 mg, 0.30 mmol) in methanol (10 mL) at −20° was treated with a stream of O_3 in O_2 for 2 min and then purged with O_2, and excess of dimethyl sulfide was added at −20°. This mixture was stirred at room temperature for 24 h, and then concentrated *in vacuo*. Preparative t.l.c. (5:95 MeOH–CH_2Cl_2) of the crude product gave **5** (44 mg, 92%, >80% α-pyranose); $\nu_{max}^{CHCl_3}$ 3450, 2925, 1120, 1050, and 1010 cm^{-1}. ^{1}H-N.m.r. data: δ 1.25 (s, 3 H, C*Me*), 1.30 (d, 3 H, $J_{6,7}$ 6 Hz, CH-*Me*), 1.76 (dd, 1 H, $J_{2a,2e}$ 14.5, $J_{1,2}$ 3.7 Hz, H-2), 2.05 (dd, 1 H, $J_{1,2}$ 0.9, $J_{2a,2e}$ 14.5 Hz, H-2), 3.03 (dd, 1 H, $J_{4,5} = J_{4,OH}$ = 9 Hz, H-4), 3.18 (d, 1 H, $J_{1,OH}$ 9.6 Hz, HO-1), 3.38 (s, 1 H, COH), 3.90 (m, 1 H, H-5), 4.18 (d, 1 H, $J_{4,OH}$ 6.6 Hz, HO-4), 5.20 (dd, $J_{1,2}$ 3.7, $J_{1,2}$ 1 Hz, H-1).

*Methyl 2,6-dideoxy-3-C-methyl-α-*ribo-*hexopyranoside*. — Triol **10** (133 mg, 0.83 mmol) was ozonized by the procedure described above to give mycarose. A solution of the crude product in methanolic 0.05M acetyl chloride (5 mL) was stirred for 1 h at 23°, filtered through Dowex 1-X8 (Na^+) resin (20 g) using methanol (100 mL), and concentrated. The crude product was purified by flash column chromatography (2:98 MeOH–CH_2Cl_2) on silica gel (20 g) to give the β-pyranoside (69 mg, 47%), R_F 0.25; ν_{max} 3450, 2960, 2850, 1160, and 1080 cm^{-1}; (the α-pyranoside, R_F 0.50, was lost due to volatility under high vacuum). ^{1}H-N.m.r. data: δ 1.27 (s, 3 H, CMe), 1.30 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 1.55 (dd, 1 H, $J_{1\,2a}$ 9.6, $J_{2a,2e}$ 13.6 Hz, H-2*a*), 1.92 (bs, 2 H, HO-3,4), 1.98 (dd, 1 H, $J_{1,2e}$ 1.9, $J_{2a,2e}$ 13.9 Hz, H-2*e*), 3.04 (bd, 1 H, $J_{4,5}$ 9 Hz, H-4), 3.46 (s, 3 H, OMe), 3.59 (dq, 1 H, $J_{5,6}$ 6.2, $J_{4,5}$ 9.4 Hz, H-5), 4.76 (dd, 1 H, $J_{1,2a}$ 9.7, $J_{1,2e}$ 1.9 Hz, H-1).

A solution of the β-pyranoside (69 mg, 0.39 mmol) in methanolic 0.05M acetyl chloride (5 mL) was allowed to equilibrate for 2.5 h and then worked-up and chromatographed as described above, to give the β-pyranoside (40 mg) and the α-pyranoside (16 mg, care being taken to avoid sublimation); ν_{max} 3490, 2940, 2840, 1160, 1130, and 1050 cm^{-1}. The n.m.r. spectrum of methyl α-mycaroside was identical to that previously published[4b]. ^{1}H-N.m.r. data: δ 1.27 (s, 3 H, CMe), 1.30 (d, 3 H, $J_{5,6}$ 9 Hz, CH*Me*), 1.80 (dd, 1 H, $J_{2a,2e}$ 15.3, $J_{1,2}$ 4.4 Hz, H-2), 2.03 (dd, 1 H, $J_{2a,2e}$ 15.3, $J_{1,2}$ 1 Hz, H-2), 2.96 (dd, 1 H, $J_{4,OH} = J_{4,5}$ = 10.9 Hz, H-4), 3.36 (s, 3 H, OMe), 3.59 (m, 1 H, H-5), 4.75 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

2,6-Dideoxy-3-C-methyl-lyxo-*hexose* (**6**, *3-epi-axenose*) *and methyl 2,6-dideoxy-3-C-methyl-α*-lyxo-*hexopyranoside*. — Triol **11** (14 mg, 0.09 mmol) was ozonized by the procedure described above, to give **α,β-6** (89% after chromatography, ~70% of β anomer); ν_{max} 3350, 2980, 2940, 1100, 1060, and 1010 cm^{-1}. ^{1}H-N.m.r. data δ 1.20–1.33 (m, 6 H, 2 CH*Me*), 1.8 (m, 2 H, H-2), 3.13 and 3.23 (2 s, 1 H, H-4), 3.71 and 4.25 (2 q, 1 H, $J_{5,6}$ 6.7 Hz, H-5), 3.71–4.25 (b, 3 OH), 4.73 (dd, $J_{1a,2a}$ 10, $J_{1a,2e}$ 2 Hz, H-1β), and 5.34 (d, $J_{1e,2}$ 3.3 Hz, H-1α).

Crude **6** from a separate experiment (45 mg of **11**) was treated with methanolic 0.05M acetyl chloride for 12 h at room temperature. The mixture was filtered through a short column of Dowex 1-X8 (Na^+) resin, the column was washed with methanol, and the eluate was concentrated *in vacuo*. Preparative t.l.c. (1:99 MeOH–CH_2Cl_2, six developments) of the crude product gave an α,β-mixture (29 mg, 59%) of methyl glycosides (R_F 0.4 for α and 0.35 for β) and uncharacterized minor products (8 mg). Repeated chromatography of the major fraction in the same solvent system gave pure α anomer (identical with a sample provided by Garegg and Norberg[5]); $\nu_{max}^{CHCl_3}$ 3550, 3450, 2940, 2840, 1125, and 1040 cm^{-1}. ^{1}H-N.m.r. data: δ 1.26 (d, 3 H, $J_{5,6}$ 6.5 Hz, CH*Me*), 1.37 (s, 3 H, CMe), 1.72–1.87 (m, 2 H, H-2), 2.17 (d, 1 H, $J_{H,OH}$ 7.6 Hz, OH), 2.59 (s, 1 H, COH), 3.18 (d, 1 H, $J_{4,OH}$ 7.0 Hz, H-4), 3.30 (s, 3 H, OMe), 4.0 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 4.72 (d, 1 H, $J_{1,2}$ 4 Hz, H-1). Mass spectrum: *m/z* 145 (M^+ − OMe), 127, 101.

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