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SYNTHESIS OF 4,6-DIDEOXY-D- AND -L-HEXOSES FROM RACEMIC AND *meso*-DIPROPENYLGLYCOL*

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ABSTRACT

Rac- and *meso*-divinylglycols offer, *via* site-selective epoxidation, a versatile strategy for the synthesis of optically pure sugars. This is exemplified in this paper by the synthesis of 4,6-dideoxyhexoses. Starting from mono-*O*-benzyl di-(1-propenyl)glycol, readily obtained from racemic-di-1-propenylglycol[(±)-**1**] with the help of Sharpless epoxidation, the **3**D and **3**L diol-epoxides, respectively, were synthesized in enantiomeric pure form. Regioselective reductive cleavage of the epoxide ring and ozonolysis of the C–C-double bond gave 2-*O*-benzyl-4,6-dideoxy-D- and -L-*xylo*-hexose (**5**D and **5**L) respectively, in only four steps from racemate[(±)-**1**]. The transformation of compound **5**L into L-chalcose is described. Similarly, mono-*O*-benzylation of *meso*-dipropenylglycol and subsequent Sharpless epoxidation in the presence of diethyl (+)-tartrate gave selectively an L-diol-epoxide, which was transformed readily into 4,6-dideoxy-L-*lyxo*-hexose and 4,6-dideoxy-3-*O*-methyl-L-*lyxo*-hexose.

INTRODUCTION

4,6-Dideoxyhexoses are constituents of many natural products including antibiotics[2]. Above all, partially *O*-substituted derivatives are interesting target molecules, for instance chalcose (4,6-dideoxy-3-*O*-methyl-*xylo*-hexose). The known syntheses of this compound from appropriately O-protected carbohydrate precursors utilize the removal of an oxy function at C-4 and C-6, either in subsequent steps or in one-step procedures[3–7]. Also the parent compound, 4,6-dideoxy-D-*xylo*-hexose, has been obtained in this way[8–10]. *De novo*-syntheses of chalcose from achiral starting materials led to racemates[11–14].

We have developed a versatile approach for the synthesis of enantiomerically pure deoxy sugars** starting from racemic or *meso*-divinylglycols[1,15–17], where a kinetic resolution *via* a site-selective Sharpless epoxidation[19,20] plays an important

De novo-Synthesis of Carbohydrates and Related Natural Products, Part 24. For Part 23, see ref. 11.
**In addition, the pheromone *exo*-brevicomin was synthesized in this way[18].

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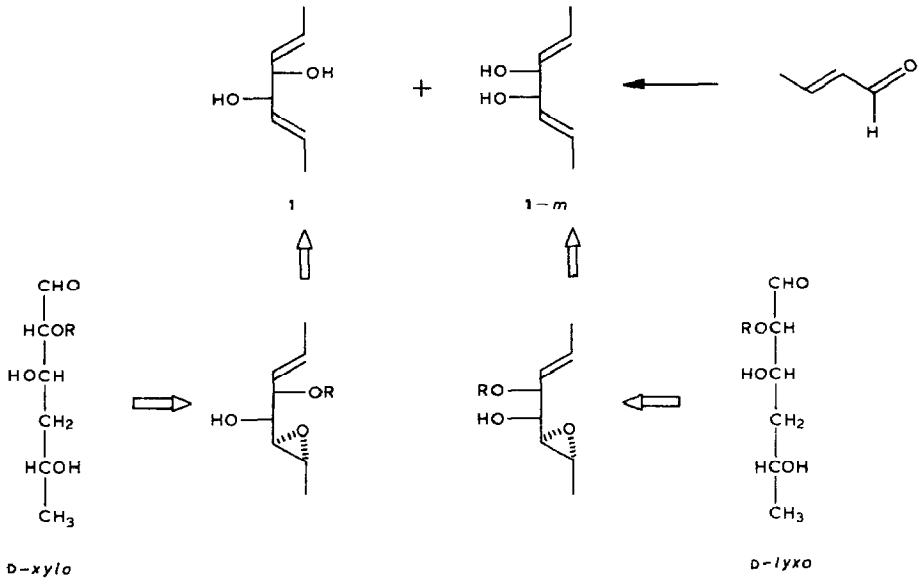


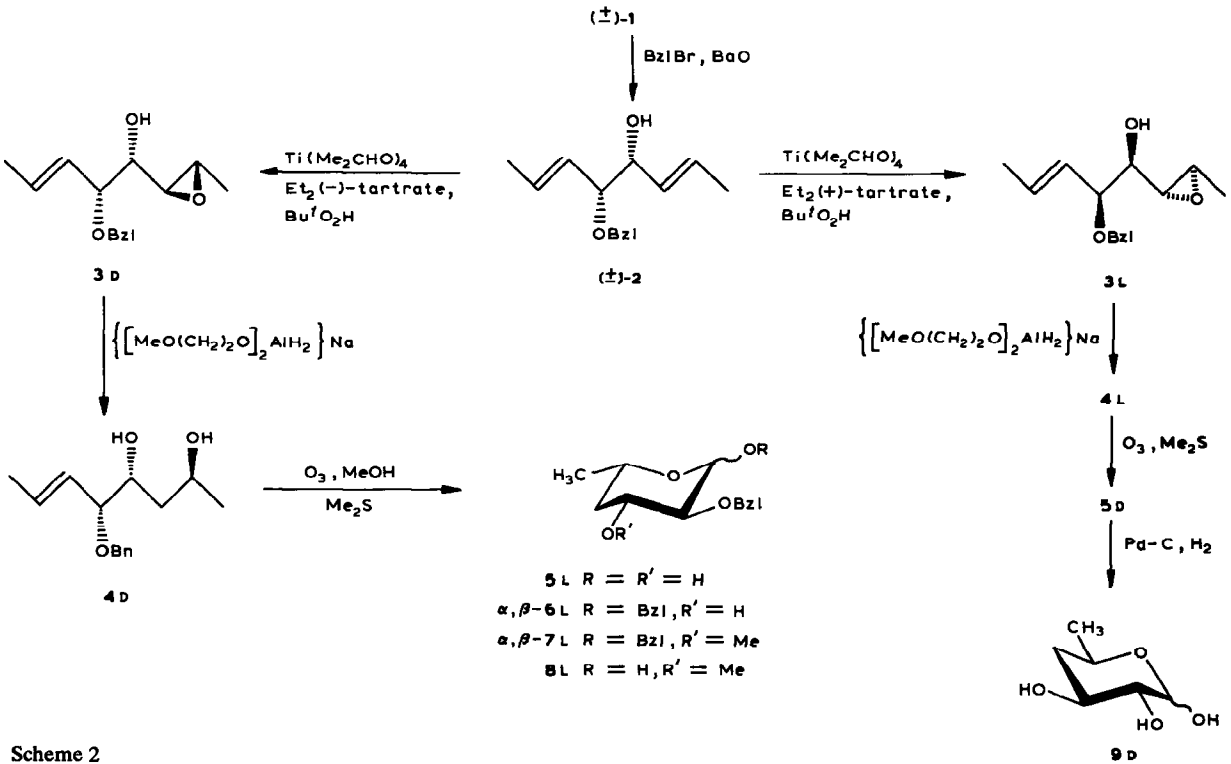
Scheme 1.

role in the control of the stereochemical structure. This method generally requires only a few steps and also gives convenient acces to partially O-protected carbohydrates. It is analyzed for the synthesis of 4,6-dideoxy sugars in the retrosynthetic Scheme 1 and exemplified by the synthesis of L-chalcose[16] (**8**L), 4,6-dideoxy-D-*xylo*-hexose (**9**D), 4,6-dideoxy-L-*lyxo*-hexose (**17**L), and 4,6-dideoxy-3-*O*-methyl-L-*lyxo*-hexose (**15**L) from racemic and *meso*-dipropenylglycol [(±)-**1** and **1**-*m*, respectively]. These starting materials were readily obtained by reductive dimerisation of crotonaldehyde[21].

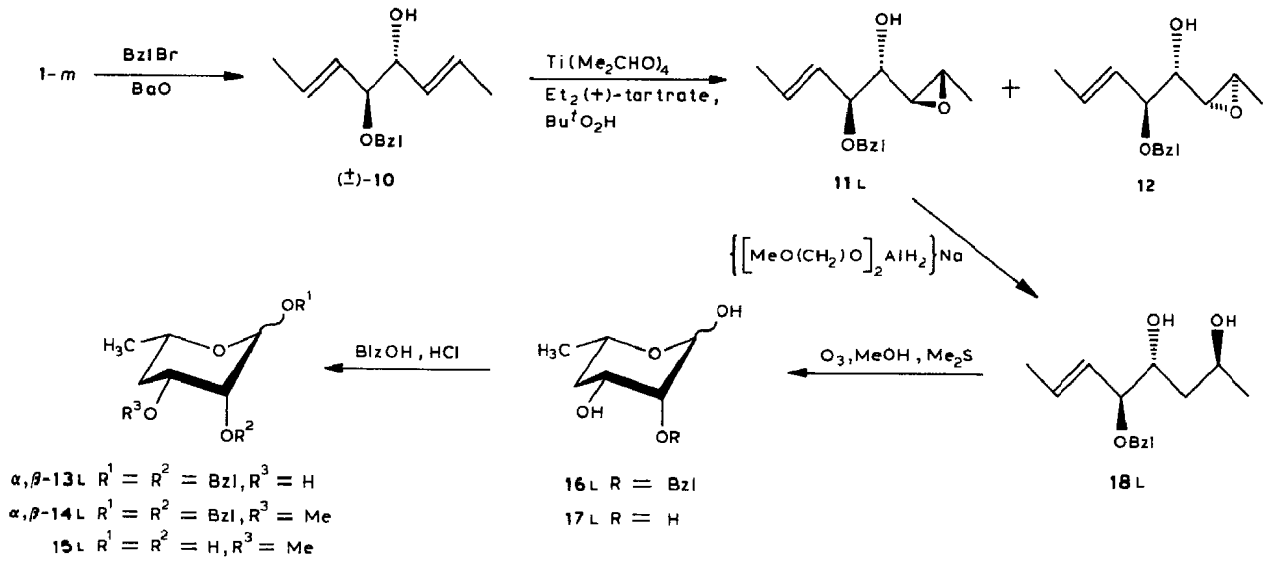
RESULTS AND DISCUSSION

For the site-selective monoepoxidation with the help of the Sharpless method[19], the divinylglycols (±)-**1** and **1**-*m* had to be transformed into the mono-*O*-benzyl protected derivatives (±)-**2** and (±)-**10**, respectively, with benzyl bromide–barium oxide and barium hydroxide. Application of the Sharpless method at −25° to the racemate (±)-**2** with diethyl (−)-tartrate gave the D-*galacto*-octenitol **3**D; the enantiomer **3**L was similarly obtained with diethyl (+)-tartrate. The structure of compounds **3**D and **3**L was finally assigned by conversion into the known 4,6-dideoxy sugars **8**L and **9**D (see below). However, the results were also in agreement with the general observations for the Sharpless method[20,22,23].

Regioselective reductive cleavage of the epoxide group of **3**D and **3**L with sodium bis(2-methoxyethoxy)aluminum hydride afforded the enantiomeric 2,4,5-triols **4**D and **4**L, respectively; an analogous opening of hydroxylalkyl-substituted


(±)-1
BzlBr, BaO
Ti(Me2CHO)4
Et2(-)-tartrate,
Bu^tO2H
Ti(Me2CHO)4
Et2(+)-tartrate,
Bu^tO2H
3D
(±)-2
3L
{[MeO(CH2)2O]2AlH2}Na
{[MeO(CH2)2O]2AlH2}Na
4L
O3, Me2S
5D
Pd-C, H2
4D
O3, MeOH
Me2S
5L R = R' = H
α,β-6L R = Bzl, R' = H
α,β-7L R = Bzl, R' = Me
8L R = H, R' = Me
9D

Scheme 2


1-m
BzlBr
BaO
OH
OBzl
(±)-10
Ti(Me2CHO)4
Et2(+)-tartrate,
BuᵗO2H
11 L
12
{[MeO(CH2)O]2AlH2}Na
18 L
O3, MeOH, Me2S
16 L R = Bzl
17 L R = H
BlzOH, HCl
α,β-13 L R1 = R2 = Bzl, R3 = H
α,β-14 L R1 = R2 = Bzl, R3 = Me
15 L R1 = R2 = H, R3 = Me

Scheme 3

epoxides has already been observed[24]. Ozonolysis of the C–C-double bond provided, in convenient four steps from (±)-**1**, the 2-*O*-benzyl-protected 4,6-dideoxy-L- and -D-*xylo*-hexoses **5**L and **5**D, respectively. Treatment of the L-isomer **5**L with benzyl alcohol–hydrochloric acid furnished an anomeric mixture of the benzyl pyranosides α,β-**6**L ($\alpha:\beta \approx 1:3$). *O*-Methylation of the unprotected hydroxyl group of this mixture with methyl iodide–sodium hydride to give α,β-**7**L and subsequent hydrogenolytic debenzylation gave L-chalcose (**8**L) in excellent yield*. The physical data of this compound were well in agreement with published data[4–6,14,25]. Hydrogenolytic debenzylation of the D-isomer **5**D gave directly 4,6-dideoxy-D-*xylo*-hexose (**9**D). Again the comparison of the physical data with those reported for this compound in the literature were in satisfactory agreement[9]. This indicated that Sharpless epoxidation of the racemate (±)-**2** gave, *via* a kinetic resolution, practically exclusively either compound **3**D or **3**L.

Application of the Sharpless method to the racemate (±)-**10** resulted not only in the expected L-*altro*-octenitol derivative **11**L but also in the diastereoisomeric *gluco* derivative** **12**. The compounds were obtained in a 3:1 ratio and were easily separated by flash chromatography. The yield of 64% for this reaction already indicated that site selectivity in the monoepoxidation of the racemate (±)-**10** was not as high as in the previous cases, which led practically to one stereoisomer only. Regioselective reductive cleavage of epoxide **11**L with sodium bis(2-methoxyethoxy)aluminum hydride afforded the L-*arabino*-triol **16**L, and subsequent ozonolysis of the C–C-double bond gave the 2-*O*-benzyl-protected 4,6-dideoxy-L-*lyxo*-hexose **16**L, again in four steps from the *meso*-compound **1**-*m*. Hydrogenolytic debenzylation of compound **14**L furnished the desired O-unprotected compound **17**L and a treatment similar to that described for L-chalcose gave, *via* compounds α,β-**16**L ($\alpha:\beta \approx 16:1$) and α,β-**17**L, the 3-*O*-methyl derivative **15**L. Compounds **15**L and **17**L had optical rotations that were not in complete agreement with the value reported[6,26] for **15**L but in agreement with the value reported[6,26] for **17**L. Thus, the structural assignment for compound **11**L was confirmed***.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter. ^{1}H-N.m.r. spectra were recorded for solutions in the solvents noted (Me_4Si, δ 0.00) with a Bruker WM 250 Cryospec instrument. R_F values refer to t.l.c. performed on silica gel (Merck) with the solvent systems noted. Column chromatography was performed under normal pressure with silica gel (Merck, 70–230 mesh ASTM and 230–400 mesh ASTM for

*D-Chalcose was obtained *via* the same route (see ref. 16).

Compound **12 is presumably a mixure of enantiomers.

***These optical rotations indicate that the enantiomeric purity of compound **11**L is at least satisfactory.

flash chromatography) and under elevated pressure with silica gel (Merck, "LiChroprep" Si 60, 40–60 μm) with the solvent systems noted. The b.p. of petroleum ether was 40–70°.

D,L-erythro- [(±)-**10**] *and* -threo-*5-O-Benzyl-2,6-octadien-4,5-diol* [(±)-**2**]. — Compound **1**-*m* or (±)-**1*** (28.44 g, 0.2 mol) and benzyl bromide (34.21 g, 0.2 mol) were dissolved in dry *N,N*-dimethylformamide (50 mL). After the addition of barium oxide (100 g) and barium hydroxide (40 g), the mixture was stirred at room temperature for three days. The solid material was filtered off through Celite and washed thoroughly with dry ether. The filtrate was once extracted with water, dried (Na_2SO_4), and evaporated. Filtration of the crude product over silica gel (3:1 petroleum ether–ether) yielded a colorless oil (21.3 g, 46%). Subsequent flash chromatography (4:1 petroleum ether–ether) gave the pure isomers (±)-**10** and (±)-**2**, respectively.

Anal. Calc. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.32; H, 8.61.

(±)-**10**. R_F 0.4 (5:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.34–7.27 (m, 5 H, C_6H_5), 5.80–5.66 (m, 2 H, H-2,7), 5.66–5.54 (m, 2 H, H-3,6), 4.62 and 4.37 (both d, 1 H each, J_{gem} 11.9 Hz, CH_2Ph), 4.11 (dd, 1 H, $J_{4,5}$ 4.1, $J_{3,4}$ 7.2 Hz, H-4), 3.73 (dd, 1 H, $J_{4,5}$ 4.1, $J_{5,6}$ 8.4 Hz, H-5), 2.3–2.1 (sb, 1 H, OH-4), 1.78 and 1.71 (both dd, 3 H each, $J_{1,2} = J_{7,8}$ 6.4, $J_{1,3} = J_{6,8}$ 1.2 Hz, H_3-1,8).

(±)-**2**: R_F 0.30 (3:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.38–7.28 (m, 5 H, C_6H_5), 5.80–5.66 (m, 2 H, H-2,7), 5.46–5.28 (m, 2 H, H-3,6), 4.63 and 4.34 (both d, each 1 H, J_{gem} 11.6 Hz, CH_2Ph), 3.98 (dd, 1 H, $J_{3,4}$ 7.0, $J_{4,5}$ 7.6 Hz, H-4), 3.59 (dd, 1 H, $J_{5,6}$ 7.9, $J_{4,5}$ 7.6 Hz, H-5), 2.80 (sb, 1 H, OH-4), 1.76 and 1.70 (both d, 3 H each, $J_{1,2} = J_{7,8}$ 6.4 Hz, H_3-1,8).

2,3-Anhydro-5-O-benzyl-1,6,7,8-tetradeoxy-L-galacto-*oct-6-enitol* (**3**L). — Titanium tetraisopropoxide (12.67 g, 44.6 mmol) and (+)-diethyl tartrate (11.24 g, 53.5 mmol) were dissolved in dry dichloromethane (450 mL) under an atmosphere of N_2 and stirred at −25° for 15 min. Stirring was continued while (±)-**2** (10.35 g, 44.6 mmol) and, after additional 15 min, 7.2M *tert*-butylhydroperoxide (26 mmol) solution in dichloromethane (3.6 mL) were added. The mixture was kept at −25° for 24 h, treated with dimethyl sulfide (11.1 g, 0.18 mmol) and, after 1 h, poured into a 5% aqueous NaF solution (900 mL) with vigorous stirring. Stirring was continued overnight, and then the suspension was centrifuged (3500 r.p.m., 30 min). The remaining solid was discarded, the liquid phases were separated, and the aqueous phase was washed five times with dichloromethane. The combined extracts were dried (Na_2SO_4) and evaporated. Column chromatography (1:1 petroleum ether–ether) yielded the starting material (5.22 g, 50%) and **3**L (3.8 g, 34%) as a colorless oil, $[\alpha]_{578}^{23}$ −47.8 (*c* 1, chloroform), R_F 0.35 (1:1 petroleum ether–ether):

*Separation of the diasteroisomers **1**-*m* and (±)-**1** was obtained by crystallization from petroleum ether at −20° to afford >90° (overall yield 40%) of the *meso*-isomer (**1**-*m*) as colorless crystals, m.p. 23°; lit.[27] m.p. 23–24°. The mother liquor, which contains ~95% of (±)-**1**, was directly used for the synthesis of (±)-**2**.

^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.40–7.26 (m, 5 H, C_6H_5), 5.82 (dq, 1 H, $J_{7,8}$ 6.4, $J_{6,7}$ 15.4 Hz, H-7), 5.50 (ddq, 1 H, $J_{6,8}$ 1.5, $J_{6,7}$ 15.4, $J_{5,6}$ 8.6 Hz, 6-H), 4.66 and 4.38 (both d, 1 H each, J_{gem} 11.8 Hz, CH_2Ph), 3.86 (dd, 1 H, $J_{4,5}$ 5.5, $J_{5,6}$ 8.6 Hz, H-5), 3.48 (ddd, $J_{4,OH-4}$ 4.3, $J_{3,4}$ 5.2, $J_{4,5}$ 5.5 Hz, H-4), 3.05 (dq, 1 H, $J_{1,2}$ 2.1, $J_{2,3}$ 2.1 Hz, H-2), 2.77 (dd, 1 H, $J_{2,3}$ 2.1, $J_{3,4}$ 5.2 Hz, H-3), 2.48 (d, 1 H, $J_{4,OH-4}$ 4.3 Hz, OH-4), 1.80 (dd, 3 H, $J_{7,8}$ 6.4, $J_{6,8}$ 1.5 Hz, H_3-8), and 1.33 (d, 3 H, $J_{1,2}$ 5.2 Hz, H_3-1).

Anal. Calc. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.35; H, 8.22.

2,3-Anhydro-5-O-benzyl-1,6,7,8-tetradeoxy-D-galacto-*oct-6-enitol* (**3D**). — The enantiomer of **3L** was synthesized by an analogous treatment of (±)-**2** with (−)-diethyl tartrate; $[\alpha]_{578}^{23}$ +46.8° (*c* 1, chloroform)*.

5-O-Benzyl-D-xylo-*6-octene-2,4,5-triol* (**4D**). — Compound **3-D** (1.2 g, 4.8 mmol) was dissolved in dry oxolane (50 mL) under an atmosphere of N_2. The mixture was cooled to 0° and 3.5M sodium bis(2-methoxyethoxy)aluminium-hydride) in toluene (3.04 mL) was added dropwise. The mixture was stirred at 0° for 1 d, excess reagent was removed by the addition of ethyl acetate, and finally water was added. The inorganic phase was extracted five times with ethyl acetate, the organic phases were combined and dried (Na_2SO_4), and the solvent was evaporated. Column chromatography of the residue (1:20 petroleum ether–ether) yielded a colorless oil (1.04 g, 86%) which crystallized, m.p. 44–45°, $[\alpha]_{578}^{23}$ −35.4° (*c* 0.24, chloroform), R_F 0.53 (1:20 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.39–7.26 (m, 5 H, C_6H_5), 5.78 (dd, 1 H, $J_{7,8}$ 6.4, $J_{6,7}$ 15.3 Hz, H-7), 5.32 (ddq, 1 H, $J_{6,8}$ 1.5, $J_{6,7}$ 15.3, $J_{5,6}$ 8.4 Hz, H-6), 4.63 and 4.33 (both d, 1 H each, J_{gem} 11.6 Hz, CH_2Ph), 4.14–4.05 (m, 1 H, H-4), 3.90–3.81 (m, 1 H, H-2), 3.64 (dd, 1 H, $J_{5,6} = J_{4,5}$ 8.4 Hz, H-5), 2.94 (d, 1 H, *J* 2.1 Hz, OH), 2.72 (d, 1 H, *J* 4.6 Hz, OH), 1.78 (dd, 3 H, $J_{7,8}$ 6.4, $J_{6,8}$ 1.5 Hz, H_3-8), 1.65–1.49 (m, 2 H, H-3,3′), and 1.20 (d, 3 H, $J_{1,2}$ 6.1 Hz, H_3-1).

Anal. Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.85; H, 8.99.

5-O-Benzyl-L-xylo-*6-octene-2,4,5-triol* (**4L**). — This compound was synthesized from **3L** as described for **4D**, m.p. 49–50°, $[\alpha]_{578}^{23}$ +31.0° (*c* 1, chloroform).

2-O-Benzyl-4,6-dideoxy-L-xylo-*hexose* (**5L**). — Compound **4-D** (840 mg, 3.36 mmol) was dissolved in 3:1 dry methanol–dichloromethane (12 mL) and ozonized with exclusion of moisture at −78° [15 min with 20 L of O_2/min ≡ 250 mg (5.2 mmol) of O_3]. The mixture was washed for 10 min with O_2-gas, and then dimethyl sulfide (2.1 g, 33.6 mmol) was added in one portion and the solution kept at −78°, 0°, and room temperature for 1 h each. After evaporation of the solvent, the residue was column chromatographed (1:20 petroleum ether–ether) to yield a colorless oil (650 mg, 81%) which crystallized, m.p. 113–114°, $[\alpha]_{578}^{23}$ −40.8° (at equil., 6 h; *c* 0.6, methanol), R_F 0.39 and 0.34 (anomers) (1:20 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.68–7.31 (m, 5 H, C_6H_5), 5.30 (dd, 0.5 H,

*The yields of **3D**, **4-L**, and **5-L** were identical with those of **3-L**, **4-D**, and **5-D**.

$J_{1,OH-1}$ 2.4, $J_{1,2}$ 3.4 Hz, H-1α), 5.04 and 4.77–4.62 (both m, 2.5 H, CH_2Ph, H-1β), 4.24–4.13 (m, 0.5 H, H-5α), 4.10–3.99 (m, 0.5 H, H-3α), 3.72–3.62 (m, 2 0.5 H, H-5β,3β), 3.32 (dd, 0.5 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.2 Hz, H-2α), 3.07 (dd, 0.5 H, $J_{2,3}$ 9.2, $J_{1,2}$ 7.9 Hz, H-2β), 2.98 (d, 0.5 H, J 2.1 Hz, OH), 2.23 (d, 0.5 H, J 2.4 Hz, OH), 2.0–1.93 (m, 2 0.5 H, H-4α,4β), 1.5–1.3 (m, 2 0.5 H, H-4'α,4'β), 1.27 (d, 1.5 H, $J_{5,6}$ 6.4 Hz, H-6β), and 1.20 (d, 1.5 H, $J_{5,6}$ 6.1 Hz, H-6α).

Anal. Calc. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.57; H, 7.66.

2-O-Benzyl-4,6-dideoxy-D-xylo-*hexose* (**5**D). — This compound was synthesized as described for **5**L; $[\alpha]_{578}^{23}$ +37.2° (*c* 1, methanol).

Benzyl 2-O-benzyl-4,6-dideoxy-α- and -β-L-xylo-*hexopyranoside* (α,β-**6**L). — Compound **5**L (610 mg, 2.6 mmol) was dissolved in dry benzyl alcohol (5 mL). The solution was saturated with dry HCl at 0° and stirred at room temperature for 4 h. BaO (5 g) oxide, suspended in water, was added to the reaction mixture in portions, until no more gas evolved. The solids were filtered off and washed with ether, and the filtrates concentrated first at 2 kPa, finally in a Kugelrohr apparatus at 50–60° and 10 Pa to remove the excess of benzyl alcohol. The residue was chromatographed (1:1 petroleum ether–ether) to yield 600 mg (70%) of the anomeric mixture as a colorless oil.

Anal. Calc. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.34. Found: C, 72.58; H, 7.29.

The anomers were separated by l.c. (elevated pressure; 1:1 petroleum ether–ether).

β-**6**L. Yield 450 mg (53%), $[\alpha]_{578}^{23}$ −78.6° (*c* 0.43, chloroform), R_F 0.20 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.46–7.29 (m, 10 H, 2 Ph), 5.02, 4.97, 4.65, 4.64 (4 d, 1 H each, J_{gem} 11.8 Hz, 2 CH_2Ph), 4.44 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.72–3.49 (m, 2 H, H-3,5), 3.18 (dd, 1 H, $J_{1,2}$ 7.6, $J_{2,3}$ 8.9 Hz, H-2), 2.33 (d, 1 H, $J_{3,OH-3}$ 1.8 Hz, OH-3), 2.15–1.93 (m, 1 H, H-4), 1.53–1.34 (m, 1 H, H-4'), and 1.30 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6).

α-**6**L. Yield 150 mg (18%), $[\alpha]_{578}^{23}$ −128.9° (*c* 1, chloroform), R_F 0.17 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.41 –7.21 (m, 10 H, 2 Ph), 4.91 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.70 and 4.58–4.46 (both m, 2 H each, 2 CH_2Ph), 4.17–4.06 (m, 1 H, H-3), 4.04–3.92 (m, 1 H, H-5), 3.29 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.5 Hz, H-2), 2.39 (sb, 1 H, OH-3), 2.10–1.98 (m, 1 H, 4-H), 1.45–1.31 (m, 1 H, H-4'), and 1.18 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

Benzyl 2-O-benzyl-4,6-dideoxy-3-O-methyl-L-xylo-*hexopyranoside* (α,β-**7**L). — To a solution of α, β-**6**L (400 mg, 1.2 mmol) in dry toluene (20 mL) and dry *N,N*-dimethylformamide (5 mL) were added methyl iodide (204 mg, 1.44 mmol) and NaH (60 mg, 2.5 mmol). The mixture was stirred at room temperature with exclusion of moisture for 10 h, and then additional NaH (60 mg, 2.5 mmol) was added and stirring continued for 14 h. Excess NaH was eliminated by treatment with methanol, and finally enough water was added to dissolve the inorganic salts. After the addition of ether (20 mL), the phases were separated and the aqueous phase was extracted three times with ether. The combined organic phases were dried (Na_2SO_4) and evaporated, and the residue filtered over silica gel (1:1

petroleum ether–ether) to give α,β-**7**L (340 mg, 83%), colorless oil, which was used without further purification, $[\alpha]_{578}^{23}$ −68.6° (*c* 1, chloroform), R_F 0.70 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.43–7.24 (m, 10 H, 2 Ph), 4.97–4.89 and 4.76–4.5 (both m, 2 H each, CH_2Ph), 4.81 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1α), 4.43 (d, 0.5 H, $J_{1,2}$ 7.3 Hz, H-1β), 3.99–3.86 (m, 0.5 H, H-5α), 3.73 (ddd, 0.5 H, $J_{2,3}$ 9.5, $J_{3,4}$ 5.2, $J_{3,4'}$ 11.3 Hz, H-3α), 3.57–3.51 (m, 2 0.5 H, H-3β,5β), 3.48 (s, 1.5 H, OCH_3α), 3.46 (s, 1.5 H, OCH_3β), 3.36 (dd, 0.5 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.5 Hz, H-2α), 3.31–3.24 (m, 0.5 H, H-2β), 2.14–2.02 (m, 1 H, H-4), 1.43–1.21 (m, 1 H, H-4'), and 1.15 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

L-*Chalcose (4,6-Dideoxy-3-*O*-methyl-*L*-xylo-hexose)* (**8**L). — Compound α,β-**7**L (260 mg, 0.76 mmol) was dissolved in dry ethyl acetate (15 mL) and hydrogenated in the presence of Pd–C (30 mg) until examination by t.l.c. showed no remaining starting material. The catalyst was filtered off and washed thoroughly with ethyl acetate, and the filtrate evaporated. Chromatography of the residue (9:1 ether–methanol) yielded **8**L (110 mg, 89%) as a colorless oil which crystallized after sublimation, m.p. 89–90°, $[\alpha]_D^{23}$ −78.0° (*c* 0.66, water; const. after 1 d), R_F 0.65 and 0.58 (anomers) (9:1 ether–methanol), lit.[4] m.p. 92–93°, $[\alpha]_D^{20}$ (D-chalcose) +75.0° (*c* 1.35, water, after 1 d). The ^{1}H-n.m.r.-data were in good agreement with those published for D-chalcose[14,25].

*4,6-Dideoxy-*D*-xylo-hexose* (**9**D). — Compound **5**D (300 mg, 1.26 mmol) was hydrogenated as described for **8**L. Chromatography (9:1 ether–methanol) yielded a colorless oil (120 mg, 64%) which crystallized from ether–methanol to give colorless crystals, m.p. 134–136°, $[\alpha]_D^{23}$ +30.0 (*c* 1, H_2O, after 2 h), R_F 0.42, 0.35 (anomers) (9:1 ether–methanol); lit.[9] m.p. 137–138°, $[\alpha]_D^{20}$ +32.5° (*c* 1.03, water, after 30 min); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 5.30 (dd, 0.5 H, $J_{1,2}$ 3.7, $J_{1,OH\text{-}1}$ 3.4 Hz, H-1α), 4.54 (dd, 0.5 H, $J_{1,2}$ 7.6, $J_{1,OH\text{-}1}$ 5.8 Hz, H-1β), 4.21–4.11 (m, 0.5 H, H-5α), 3.96–3.85 (m, 0.5 H, H-3α), 3.77–3.63 (m, 2 0.5 H, H-5β,3β), 3.50–3.36 (m, 0.5 H, H-2α), 3.50–3.36 (m, 0.5 H, H-2α), 3.26–3.19 (m, 0.5 H, H-2β), 3.01 (d, 0.5 H, $J_{1,OH\text{-}1}$ 5.8 Hz, H-1β), 2.69 (d, 0.5 H, *J* 3.1 Hz, OH), 2.48 (d, 0.5 H, *J* 2.1 Hz, OH), 2.35 (d, 0.5 H, *J* 2.8 Hz, OH), 2.27 (d, 0.5 H, *J* 2.8 Hz, OH), 2.11–1.96 (m, 1 H, H-4), 1.61–1.31 (m, 1 H, H-4'), 1.28 and 1.22 (both d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

Anal. Calc. for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.74; H, 8.02.

*2,3-Anhydro-5-*O*-benzyl-1,6,7,8-tetradeoxy-*L*-altro-oct-6-enitol* (**11**L) *and 2,3-anhydro-5-*O*-benzyl-1,6,7,8-tetradeoxy-*L*-gluco-oct-6-enitol* (**12**). — (+)-Diethyl tartrate (16.46 g, 80 mmol) and titanium tetraisopropoxide (18.90 g, 66.5 mmol) were stirred for 15 min with dry dichloromethane (650 mL) chloride under an N_2 atmosphere at −25°. Stirring was continued while (±)-**10** (15.45 g, 66.5 mmol) and, after an additional 15 min, 7.2M *tert*-butyl hydroperoxide solution in dichloromethane (9.24 mL, 66.5 mmol) was added. The mixture was kept at 25° for 2 d when t.l.c. still showed unreacted starting material. The mixture was treated with dimethyl sulfide (16.78 g, 0.27 mol) and kept at −25°. After 1 h, it was poured into 5% aqueous NaF (1 L) with vigorous stirring, and stirring was continued overnight. The suspension was centrifuged at 3500 r.p.m. for 30 min, the solids

discarded, and the liquid phases were separated. The aqueous phase was extracted five times with dichloromethane, the combined extracts were dried (Na_2SO_4), and the solvent was evaporated. The isomeric epoxides were separated by flash chromatography (1:1 petroleum ether–ether).

Anal. Calc. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.32; H, 7.99.

11L. Yield 7.9 g (48%), colorless oil, R_F 0.34 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.39–7.26 (m, 5 H, C_6H_5), 5.80 (dq, 1 H, $J_{7,8}$ 6.4, $J_{6,7}$ 12.8 Hz, H-7), 5.57 (ddq, 1 H, $J_{6,8}$ 1.5, $J_{6,7}$ 12.8, $J_{5,6}$ 8.6 Hz, H-6), 4.65 and 4.37 (both d, 1 H each, J_{gem} 11.9 Hz, CH_2Ph), 3.86 (dd, 1 H, $J_{5,6}$ 8.6, $J_{4,5}$ 4.6 Hz, H-5), 3.69 (ddd, 1 H, $J_{4,5}$ 4.6, $J_{3,4}$ 8.6, $J_{4,OH-4}$ 3.7 Hz, H-4), 3.02 (dq, 1 H, $J_{1,2}$ 5.2, $J_{2,3}$ 2.4 Hz, H-2), 2.85 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 8.6 Hz, H-3), 2.23 (d, 1 H, $J_{4,OH-4}$ 3.7 Hz, OH-4), 1.81 (dd, 3 H, $J_{7,8}$ 6.4, $J_{6,8}$ 1.5 Hz, H-8), and 1.29 (d, 3 H, $J_{1,2}$ 5.2 Hz, H-1).

12. Yield 2.6 g (16%), colorless oil, R_F 0.27 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5 H, C_6H_5), 5.82 (dd, 1 H, $J_{6,7}$ 12.8, $J_{7,8}$ 6.4 Hz, H-7), 5.48 (ddq, 1 H, $J_{6,8}$ 1.5, $J_{6,7}$ 12.8, $J_{5,6}$ 8.2 Hz, H-6), 4.65 and 4.38 (both d, 1 H each, J_{gem} 11.9 Hz, CH_2Ph), 3.84 (dd, 1 H, $J_{5,6}$ 8.2, $J_{4,5}$ 6.1 Hz, H-5), 3.50 (ddd, 1 H, $J_{4,5}$ 6.1, $J_{3,4}$ 4.6, $J_{4,OH-4}$ 6.7 Hz, H-4), 3.01 (dq, 1 H, $J_{2,3}$ 2.4, $J_{1,2}$ 5.2 Hz, H-2), 2.93 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 4.6 Hz, H-3), 2.15 (d, 1 H, $J_{4,OH-4}$ 6.7 Hz, OH-4), 1.80 (dd, 3 H, $J_{7,8}$ 6.4, $J_{6,8}$ 1.5 Hz, H_3-8), and 1.32 (d, 3 H, $J_{1,2}$ 5.2 Hz, H_3-1).

5-O-Benzyl-L-arabino-*6-octen-2,4,5-triol* (**18**L). — Compound **11**L (3.98 g, 16.03 mmol) was treated with a solution (10 mL) of sodium bis(2-methoxyethoxy)aluminum hydride (35 mmol) in dry oxolane (160 mL) at 0° as described for **4**D. Chromatography of the crude product (1:20 petroleum ether–ether) yielded a waxy solid (3.51 g, 88%), $[\alpha]_{578}^{23}$ +53.6° (*c* 1, chloroform), R_F 0.38 (1:20 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.39–7.26 (m, 5 H, C_6H_5), 5.77 (dq, 1 H, $J_{6,7}$ 15.4, $J_{7,8}$ 6.4 Hz, H-7), 5.47 (ddq, 1 H, $J_{6,7}$ 15.4, $J_{5,6}$ 8.6, $J_{6,8}$ 1.5 Hz, H-6), 4.62 and 4.35 (both d, 1 H each, J_{gem} 11.8 CH_2Ph), 4.11 (m, 1 H, H-2), 4.00 (m, 1 H, H-4), 3.69 (dd, 1 H, $J_{5,6}$ 8.6, $J_{4,5}$ 4.9 Hz, H-5), 2.42 and 2.35 (both d, 1 H each, *J* 3.7 Hz, OH), 1.80 (dd, 3 H, $J_{7,8}$ 6.4, $J_{6,8}$ 1.5 Hz, H-8), 1.73–1.43 (m, 2 H, H-3,3'), and 1.22 (d, 3 H, $J_{1,2}$ 6.4 Hz, H_3-1).

Anal. Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.77; H, 8.75.

2-O-Benzyl-4,6-dideoxy-L-lyxo-*hexose* (**16**L). — Compound **18**L (3.5 g, 14.02 mmol) was dissolved in a mixture of dry methanol (30 mL) and dry dichloromethane (10 mL), and treated with O_3 as described for **5**L. Chromatography (1:20 petroleum ether–ether) gave **16**L as colorles crystals (3.0 g, 90%), m.p. 111–112°, R_F 0.36 (1:20 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.68–7.26 (m, 5 H, C_6H_5), 5.35 (br., 1 H, H-1), 4.75 and 4.58 (both d, 1 H each, J_{gem} 11.8 Hz, CH_2Ph), 4.12–3.94 (m, 2 H, H-3,5), 3.59 (br., 1 H, H-2), 2.32 (d, 1 H, *J* 3.4 Hz, OH), 2.11 (d, 1 H, *J* 11.0, OH), 1.80–1.61 and 1.56–1.51 (both m, 1 H each, H-4,4'), and 1.22 (d, 3 H, $J_{5,6}$ 6.1 Hz, H_3-6).

Anal. Calc. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.22; H, 7.30.

4,6-Dideoxy-L-lyxo-*hexose* (**17**L). — Compound **16**L (240 mg, 1.0 mmol) was

hydrogenated in dry ethyl acetate (10 mL) with Pd–C (30 mg) as catalyst until t.l.c. showed no remaining starting material. The catalyst was filtered off and washed thoroughly with ethyl acetate, the filtrates were evaporated, and the residue was chromatographed (9:1 ether–methanol) to give **15**L as colorless crystals (135 mg, 91%), m.p. 129–134°, $[\alpha]_D^{20}$ −3.5° (*c* 0.38, water, after 5 h), R_F 0.37 (9:1 ether–methanol); lit.[6,26] $[\alpha]_D^{20}$ −2.8° (*c* 0.5, water, const.); ^{1}H-n.m.r. (150 MHz, $CDCl_3$): δ 5.13 (br. s, 0.5 H, H-1a), 4.60 (sb, 0.5 H, H-1b), 4.14–3.96 (m, 2 0.5 H, H-3b,5b), 3.73–3.65 (m, 1 H, H-2), 3.56–3.35 (m, 2 0.5 H, H-3a,5a), 1.71–1.45 (m, 2 H, H-4,4′), 1.27 and 1.23 (both d, 3 H, $J_{5,6}$ 6.1 Hz, H_3-6).

Anal. Calc. for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.27; H, 8.27.

*Benzyl 2-O-benzyl-4,6-dideoxy-α- and -β-*L*-lyxo-hexopyranoside* (**α,β-13**L). — Compound **16**L (240 mg, 1.0 mmol) was dissolved in dry benzyl alcohol (5 mL) and treated with HCl as described for **α,β-6**L. After purification of the product by column chromatography (1:1 petroleum ether–ether) to yield a colorless oil (280 mg, 85%), the anomers were separated by l.c. (under elevated pressure and same solvent).

α-13L. Colorless crystals, m.p. 47–48°. $[\alpha]_{578}^{23}$ −65.9° (*c* 1, methanol), R_F 0.34 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.39–7.26 (m, 10 H, 2 Ph), 5.00 (br. s, 1 H, H-1), 4.72, 4.71, 4.52, 4.47 (4 d, 1 H each, J_{gem} 11.9 Hz, 2 CH_2Ph), 4.05–3.82 (m, 2 H, H-3,5), 3.58 (br., 1 H, $J_{2,3}$ 2.1 Hz, H-2), 2.12 (d, 1 H, $J_{3,OH\text{-}3}$ 11.0 Hz, OH-3), 1.75 (m, 1 H, $J_{4,4'}$ 12.2 Hz, H-4), 1.58 (m, 1 H, $J_{4,4'}$ 12.2 Hz, H-4′), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

Anal. Calc. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.98; H, 7.31.

β-13L. Colorless crystals, m.p. 104–106°, $[\alpha]_{578}^{23}$ +10.5° (*c* 1, chloroform), R_F 0.27 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.38–7.26 (m, 10 H, 2 Ph), 5.15, 5.03, 4.65, 4.61 (4 d, 1 H each, J_{gem} 12.1 Hz, 2 CH_2Ph), 4.42 (d, 1 H, $J_{1,2}$ 0.6 Hz, H-1), 3.71–3.41 (m, 2 H, H-3,5), 2.19 (d, 1 H, $J_{3,OH\text{-}3}$ 11.0 Hz, OH-3), 1.72 (mc*, 1 H, H-4), 1.43 (mc, 1 H, H-4′), and 1.32 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

Anal. Calc. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.53; H, 7.47.

*Benzyl 2-O-benzyl-4,6-dideoxy-3-O-methyl-α- and -β-*L*-lyxo-hexopyranoside* (**α,β-14**L). — Compound **α,β-13**L (500 mg, 1.52 mmol) was dissolved in a mixture of dry toluene (20 mL) and dry *N,N*-dimethylformamide (5 mL), and treated with methyl iodide (250 mg, 1.74 mmol) and (NaH) (2 × 60 mg, 5 mmol) as described for **α,β-7**L. The crude product was purified by column chromatography (2:1 petroleum ether–ether) to give a colorless oil (440 mg, 85%).

Anal. Calc. for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.49; H, 7.63.

The anomers were separated by l.c. at elevated pressure (2:1 petroleum ether–ether).

α-14L. Yield 400 mg (77%), colorless oil, $[\alpha]_{578}^{23}$ −46.5° (*c* 1, chloroform), R_F

*mc, multiplet centered at.

0.62 (1:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.37–7.21 (m, 10 H, C_6H_5), 4.94 (br. s, 1 H, H-1), 4.74, 4.69, 4.67, 4.44, (4 d, 1 H each, J_{gem} 12.4 Hz, 2 CH_2Ph), 3.89 (mc, 1 H, H-5), 3.68–3.59 (m, 2 H, H-2,3), 3.31 (s, 3 H, OCH_3), 1.87–1.75 (m, 2 H, H-2,3), 3.31 (s, 3 H, OCH_3), 1.87–1.75 (m, 2 H, H-4,4'), and 1.25 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

β-14L. 40 mg (7.7%), colorless oil, $[\alpha]_{578}^{23}$ +72.0° (*c* 1, chloroform), R_F 0.29 (2:1 petroleum ether–ether); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.37–7.21 (m, 10 H, 2 Ph), 4.94 (br. s, 1 H, H-1), 4.74, 4.69, 4.67, 4.44 (4 d, 1 H each, J_{gem} 12.3 Hz, 2 CH_2Ph), 3.89 (mc, 1 H, H-5), 3.68–3.59 (m, 2 H, H-2,3), 3.31 (s, 3 H, OCH_3), 1.87–1.75 (m, 2 H, H-4,4'), and 1.25 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

4,6-Dideoxy-3-O-methyl-L-lyxo-*hexose* (**15L**). — Compound **α,β-14L** (220 mg, 0.64 mmol) was dissolved in dry ethyl acetate (15 mL) and hydrogenated in the presence of Pd–C (30 mg) until t.l.c. examination showed no remaining starting material. The catalyst was filtered off and washed thoroughly with ethyl acetate, and the filtrates were evaporated. The crude product was chromatographed (9:1 ether–methanol) to yield a crystalline solid. Recrystallization from ether–methanol gave colorless crystals (84 mg, 77%), m.p. 104–106°, $[\alpha]_D^{23}$ +5.8° (*c* 1, water, after 6 h), R_F 0.59 (9:1 ether–methanol); lit.[6,26] m.p. 106–107°, $[\alpha]_D^{20}$ +9.9° (*c* 0.9, water); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 5.31 (br. s, 1 H, H-1), 4.17–4.04 (m, 1 H, H-5), 3.95 (br. d, 1 H, $J_{2,3}$ 2.4 Hz, H-2), 3.71–3.63 (m, 1 H, H-3), 3.4 (s, 3 H, OCH_3), 2.68 (d, 1 H, *J* 3.4 Hz, OH), 2.25 (d, 1 H, *J* 2.4 Hz, OH), 1.82–1.73 (m, 1 H, H-4), 1.64–1.45 (m, 1 H, H-4'), and 1.24 (d, 3 H, $J_{5,6}$ 6.4 Hz, H_3-6).

Anal. Calc. for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.34; H, 8.56.

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REFERENCES

1 U. KÜFNER AND R. R. SCHMIDT, *Justus Liebigs Ann. Chem.*, (1986) 1610–1620.
2 J. S. BRIMACOMBE, *Angew. Chem.*, 83 (1971) 261–300; *Angew. Chem., Int. Ed. Engl.*, 10 (1971) 236–275.
3 S. MCNALLY AND W. G. OVEREND, *Chem. Ind. (London)*, (1964) 2021; S. MCNALLY, M. STACEY, J. M. WEBBER, AND J. H. WESTWOOD, *J. Chem. Soc.*, (1965) 2319–2322.
4 N. K. KOCHETKOV AND A. J. USOV, *Tetrahedron Lett.*, (1963) 519–522.
5 B. T. LAWTON, D. J. WARD, W. A. SZAREK, AND J. K. N. JONES, *Can. J. Chem.*, 47 (1969) 2899–2901.
6 K. KEFURT, Z. KEFURTOVÁ, AND J. JARÝ, *Coll. Czech. Chem. Commun.*, 38 (1972) 2627–2632.
7 H. REDLICH AND W. ROY, *Carbohydr. Res.*, 68 (1979) 275–285.
8 E. J. HEDGELEY, W. G. OVEREND, AND R. A. C. RAMIE, *J. Chem. Soc.*, (1963) 4701–4711; K. CAPEK, J. NEMEC, AND J. JARÝ, *Coll. Czech. Chem. Commun.*, 33 (1967) 1758–1767.
9 J. HILL, L. HOUGH, AND A. C. RICHARDSON, *Proc. Chem. Soc., London*, (1963) 314–315.

10 J. HILL, L. HOUGH, AND A. C. RICHARDSON, *Carbohydr. Res.*, 8 (1968) 19–28; G. SIEWERT AND O. WESTPHAL, *Justus Liebigs Ann. Chem.*, 720 (1968) 161–170; B. T. LAWTON, W. A. SZAREK, AND J. K. N. JONES, *Carbohydr. Res.*, 14 (1970) 255–258.
11 R. M. SRIVASTAVA AND R. K. BROWN, *Can. J. Chem.*, 48 (1970) 830–837.
12 K. TORSELL AND M. P. TYAGI, *Acta Chem. Scand.*, 331 (1977) 7–10.
13 A. BANASZEK AND A. ZAMOJSKI, *Rocz. Chem.*, 45 (1971) 391–397.
14 S. DANISHEFSKY AND J. F. KERWIN, *J. Org. Chem.*, 47 (1982) 1597–1598.
15 U. KÜFNER, Dissertation, Universität Konstanz, 1986.
16 U. KÜFNER AND R. R. SCHMIDT, *Angew. Chem.*, 98 (1986) 90–91; *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 89.
17 U. KÜFNER AND R. R. SCHMIDT, *Justus Liebigs Ann. Chem.*, (1986) 1600–1609.
18 U. KÜFNER AND R. R. SCHMIDT, *Synthesis*, (1985) 1060–1062.
19 T. KATSUKI AND K. B. SHARPLESS, *J. Am. Chem. Soc.*, 102 (1980) 5974–5976.
20 V. S. MARTIN, S. S. WOODARD, T. KATSUKI, Y. YAMADA, M. IKEDA, AND K. B. SHARPLESS, *J. Am. Chem. Soc.*, 103 (1981) 6237–6239.
21 W. G. YOUNG, L. LEVANAS, AND Z. JESAITIS, *J. Am. Chem. Soc.*, 58 (1936) 2274–2276.
22 K. B. SHARPLESS, S. S. WOODARD, AND M. G. FINN, *Pure Appl. Chem.*, 55 (1983) 1823–1826.
23 S. Y. KOO, A. W. M. LEE, S. MASAMUNE, L. A. REED, K. B. SHARPLESS, AND F. J. WALKER, *Science*, 220 (1983) 949–951.
24 F. M. FINAN AND Y. KISHI, *Tetrahedron Lett.*, 23 (1982) 2719–2722; S. M. VITI, *ibid.*, 23 (1982) 4541–4544.
25 P. W. K. KOO, H. W. DION, AND L. F. JOHNSON, *J. Am. Chem. Soc.*, 84 (1962) 1066–1067.
26 K. KEFURT, Z. KEFURTOVÁ, AND J. JARÝ, *Coll. Czech. Chem. Commun.*, 36 (1971) 1701–1704.
27 W. STORCK AND G. MANECKE, *Makromol. Chem.*, 110 (1967) 207–221; J. WEIMANN, G. DANA, S. L. THI-THUAU, AND M. BRAMI, *C.R. Hebd. Séances Acad. Sci., Ser. C.*, 258 (1964) 3724–3727.