Carbohydrate Research, 200 (1990) 209–225
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Stereocontrolled synthesis of lankanolide from 1,6-anhydro-β-D-glucopyranose (levoglucosan): 1, synthesis of the C-1/7 and C-8/15 Segments

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(Received May 23rd, 1989; accepted for correspondence, August 31st, 1989)

ABSTRACT

A scheme has been designed for the stereocontrolled synthesis of lankanolide, the aglycon of lankamycin. Synthesis of its C-1/7 and C-8/15 segments has been accomplished starting from 1,6-anhydro-2,4-dideoxy-2,4-di-*C*-methyl-β-D-glucopyranose.

INTRODUCTION

Macrolide antibiotics, especially 14-membered examples [*e.g.*, erythromycins A and B, oleandomycin, lankamycin (**1**)], which are important in practical medicine, have become attractive targets for total synthesis[1]. Of the compounds synthesised to date can be mentioned erythromycin A[2-4], aglycons of erythromycins A[5-9] and B[10,11], and 6-deoxyerythronolide B[12]. Recent studies have been aimed at stereocontrolled syntheses of lankanolide[13] (**2**) and oleandonolide[14,15].

Our synthesis strategy[16], which involved sugars as precursors for erythronolides A (**11**) and B (**12**), provided the basis for an approach to lankanolide (**2**) taking into account its structural similarity to **11** and **12** which, in turn, is associated with the pathways of biosynthesis.

We now present the retrosynthetic analysis of lankanolide (**2**), and report the synthesis of its C-1/7 and C-8/15 segments from 1,6-anhydro-2,4-dideoxy-2,4-di-*C*-methyl-β-D-glucopyranose which is available easily (overall yield of 38%) from levoglucosan in 5 steps[17].

RESULTS AND DISCUSSION

Macrolactonisation of lankanolide seco-acid followed by transformation of the macrolactone into lankanolide is suggested by the procedure applied[9] in the synthesis of erythronolide A and B. The key intermediate for this approach is the seco-acid derivative **3**. Successive retrosynthetic transformation of this molecule yields initially **4** then, following disconnection of the C-7–C-8 bond, two keys segments, namely, the aldehyde

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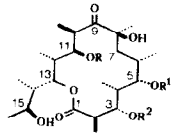
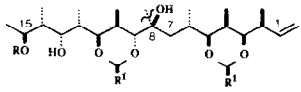
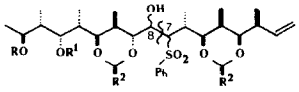


1 R = Ac, R^1, R^2 = H,OOR

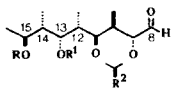
2 R = R^1 = R^2 = H



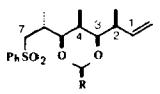
3 R = Bn, R^1 = *p*-MeOPh



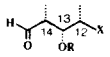
4 R = Bn, R^1 = ^{t}BuMe$_2$Si, R^2 = *p*-MeOPh



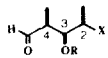
5 R = Bn, R^1 = ^{t}BuMe$_2$Si, R^2 = *p*-MeOPh



6 R = *p*-MeOPh



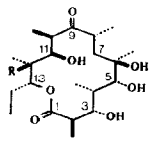
7 R = *p*-MeOBn



8 R = *p*-MeOBn

9

10



11 R = OH

12 R = H

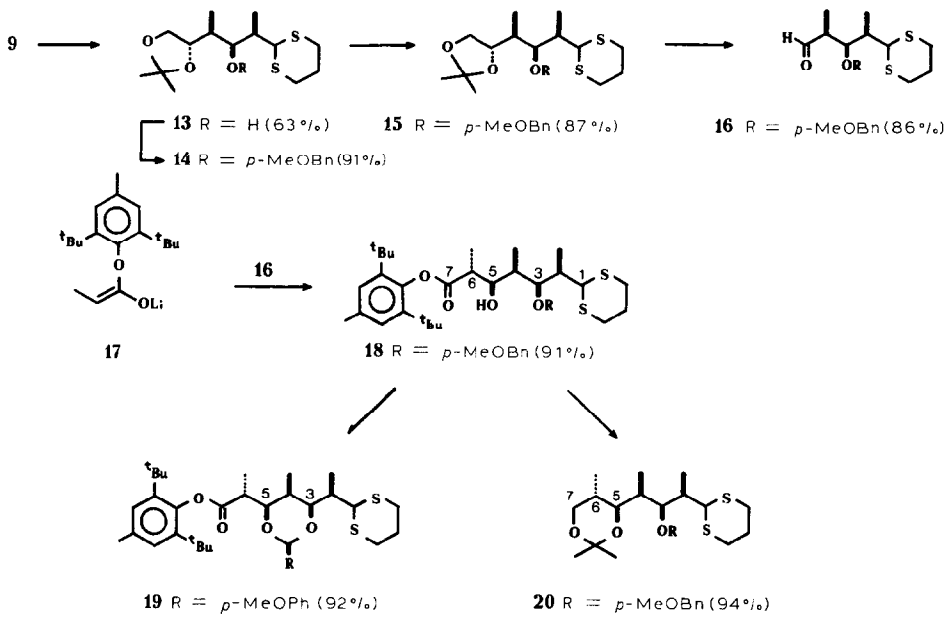
5 (C-8/15) and the sulfone **6** (C-1/7). Similar retrosynthesis analysis of lankanolide has been performed by Paterson[13].

The starting point for further disassembly of segments **5** and **6** was the stereochemical identity therein and, consequently, in **2**, of the C-2/4 and C-12/14 moieties, which correspond to the C-2/4 moiety of the bicyclic derivative **9**. Compound **9**, easily accessible from levoglucosan[17] (**10**), was employed in the synthesis[9] of erythronolides A and B.

The stereoselective approach to lankanolide (**2**) requires extension of the C-2/4 segment **8** derived from **9** to give the C-1/7 segment as a sulfone **6**, and, likewise, of the C-12/14 segment **7**, also obtainable from **9**, to give the C-8/15 segment as the aldehyde **5** followed by coupling and creation of the desired stereochemistry at the tertiary centre C-8. This sequence would result in assembly of the carbon chain of the target seco-acid derivative **3**.

Synthesis of the C-1/7 segment. — As the key intermediate in the synthesis of the segments **5** and **6**, the aldehyde **16** was chosen, which was obtained from **9** as follows. Reaction of **9** with propane-1,3-dithiol–boron trifluoride etherate and *O*-isopropylidenation of the resulting triol yielded the alcohol **13**, which was converted into the *p*-methoxybenzyl derivative **14**. *O*-De-isopropylidenation of **14** (→**15**) followed by glycol cleavage gave **16** (43% from **9**).

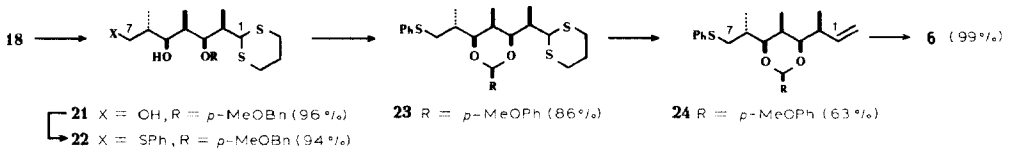
Transformation of the aldehyde **16** into the C-1/7 segment **6** requires elongation of the carbon chain with the formation of the 4,5-*syn*,5,6-*anti*-configuration of the new chiral centres. Reaction of the aldehyde derivative, analogous to **16**, with the enolate **17** gave[13] a product with the above configuration. Literature data[18–20] on the aldol addition



of enolates to chiral β-alkoxyaldehydes revealed **17** to be an exceptional and almost unique reagent which would afford mainly the product with the above stereochemistry.

In fact, addition of **17** to **16** gave the required aldol **18** as the sole product (92%). The stereochemistry of the newly formed centres, C-5 and C-6, in **18** was indicated by the ^{1}H-n.m.r. data for the derived cyclic acetals **23** and **24** [**23**: n.O.e. (H_{acetal}) H-3 8.3%, and (H_{acetal}) H-5 7.1%; **24**: $J_{5,6}$ 10.5, $J_{6,7a}$ 11.5, $J_{6,7e}$ 5 Hz]. Compound **23** was obtained by 5,6-dichloro-2,3-dicyano-1,4-benzoquinone (DDQ)-induced oxidative cyclisation[21] of **18** and **24** was prepared by reduction of the ester function followed by acetonation of the resulting diol **21**.

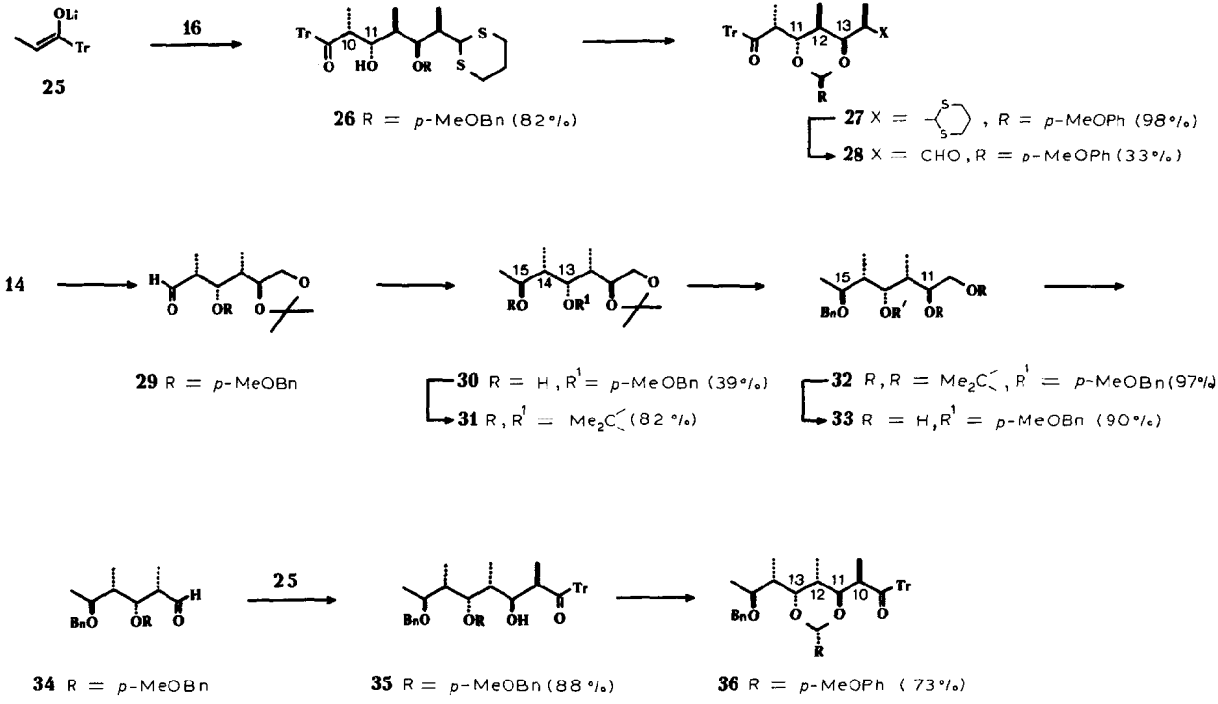
Transformation of **21** into the C-1/7 segment **6** was performed by standard methods employed[9] in the synthesis of erythronolides A and B, which involved conversion[22] into the phenylthio derivative **22**, oxidative acetalation[21] of the *p*-methoxybenzyl ether (→**23**), removal of the dithioacetal group, conversion of the resulting aldehyde into the methylene derivative **24** by a Wittig reaction, and then *S*-oxidation to give the sulfone **6**.

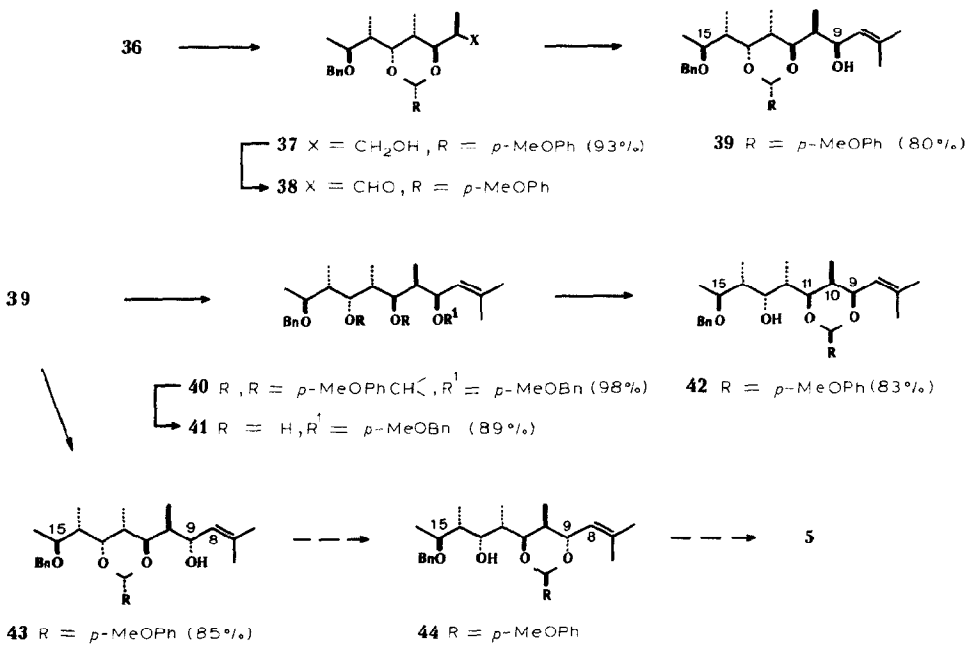


Synthesis of the C-8/15 segment. — The new chiral centres C-10 and C-11 of the C-8/15 segment of lankanolide with the required configuration could be generated from the aldehyde **16** by the use of a reagent that effected *syn*-simple/*anti*-diastereofacial stereoselectivity in the aldol reaction. Such a reagent is the lithium enolate of ethyl trityl ketone **25**[9,23] which reacted with **16** to afford the aldol **26** as the sole product. The *syn*-orientation at C-10 and C-11 in **26** was established by the ^{1}H-n.m.r. data ($J_{10,11}$ 0 Hz), and the *anti*-configuration at C-11 and C-12 followed from those of the cyclic acetal **27** prepared from **26** by DDQ-induced cyclisation under neutral conditions[21] [n.O.e (H_{acetal}) H-13 −9%, (H_{acetal}) H-10 −7.8%, (H_{acetal}) Me-10 −3.4%].

Selective hydrolysis of the dithioacetal function in **27** gave only 33% of **28** (*cf.* the high yield of aldehyde from **23**). Therefore, this critical step was shifted towards the beginning of the synthesis sequence even though dethioacetalation of an early intermediate **14** was not very efficient. Aldehyde **29**, derived from **14**, was treated[25] with lithium dimethylcuprate to give the alcohol **30** (39% from **14**). The configuration at C-15 in **30** was deduced from ^{1}H-n.m.r. data ($J_{14,15}$ 8, $J_{13,14}$ 4.5 Hz; n.O.e. between Me-15 and both H-13 and the CMe_2 group) for the bicyclic derivative **31**, prepared by successive removal of the *p*-methoxybenzyl group and acetalation.

Transformation of **30** into the intermediate aldehyde **38** was performed in a routine sequence. Benzylation of **30** (→**32**) followed by mild acid hydrolysis of the *O*-isopropylidene group and cleavage of the resulting glycol **33** with lead tetra-acetate afforded the aldehyde **34**. Treatment of **34** with the lithium enolate (**25**) of ethyl trityl


OLi
Tr
25
16
Tr
10
11
HO
OR
S
S
26 R = p-MeOBn (82%)
Tr
11
12
13
X
O
O
O
R
27 X = S S , R = p-MeOPh (98%)
28 X = CHO, R = p-MeOPh (33%)
14
H
O
OR
O
29 R = p-MeOBn
15
14
13
RO
OR1
O
30 R = H, R1 = p-MeOBn (39%)
31 R, R1 = Me2C (82%)
15
11
BnO
OR'
OR
32 R, R = Me2C, R1 = p-MeOBn (97%)
33 R = H, R1 = p-MeOBn (90%)
BnO
OR
H
O
34 R = p-MeOBn
25
BnO
OR
OH
Tr
O
35 R = p-MeOBn (88%)
13
11
12
10
BnO
O
O
O
Tr
R
36 R = p-MeOPh (73%)



ketone gave, as anticipated (*cf.* the transformation **16**→**26**), **35** (88% from **33**) as the only product. The *anti*-orientation of substituents at C-11 and C-12 in **33** followed from ^{1}H-n.m.r. data [n.O.e. (H_{acetal}) H-13 −9%; $J_{11,12}$ 0, $J_{12,13}$ 2 Hz] for the cyclic acetal **36** derived therefrom by the action of DDQ under neutral conditions[21]. That the substituents at C-10 and C-11 in **35** were *syn*-oriented was established after later transformations (see **42**).

Reductive cleavage[23] of the TrCO group in **36** gave the primary alcohol **37** which was oxidised to the aldehyde **38**. Addition of lithium di(2-methylpropenyl)cuprate to **38** proceeded stereospecifically to give **39**, the stereochemistry of C-9 in which was the opposite of that required and anticipated[24]. This was indicated by ^{1}H-n.m.r. data for the cyclic derivative **42** prepared from **39** as follows: HO-9 was protected as the *p*-methoxybenzyl ether (→**40**), the *p*-methoxybenzylidene group was hydrolysed, and the resulting diol **41** was treated with DDQ under neutral conditions[21] to give **42** [$J_{9,10} = J_{10,11} = 2$ Hz; n.O.e. (H_{acetal}) H-9 2%, (H_{acetal}) H-11 3%].

Compound **39** was epimerised at C-9 by the Mitsunobu reaction[25] to give the alcohol **43**, the configurations of the chiral centres in which, including that of C-9, correspond to those of the C-8/15 segment of lankanolide.

The use of **6** and **43** (as a precursor for the aldehyde **5**) in the total synthesis of lankanolide is in progress.

EXPERIMENTAL

Optical rotations were measured on solutions in chloroform with a JASCO DIP-360 polarimeter. ^{1}H-N.m.r. spectra were recorded with a Bruker WM-250 instrument. N.O.e. studies, for solutions degassed with argon, were performed according to the TOE procedure (the difference version[26]). The numbering used in the ^{1}H-n.m.r. data corresponds to that in the respective formulae. Reactions were monitored, and the purity of products was assessed, by t.l.c. on silica gel (Merck). H.p.l.c. was performed on a column of "Silpearl" silica gel (25–40 μm), using an isocratic regime with a Knauer 88.00 refractometer. Reactions sensitive toward oxygen and moisture were carried out under argon. Solvents were dried under argon with suitable dehydrating agents.

*2,4-Dideoxy-5,6-*O*-isopropylidene-2,4-di-*C*-methyl-*D*-glucose trimethylene dithioacetal* (**13**). — A solution of 1,6-anhydro-2,4-dideoxy-2,4-di-*C*-methyl-β-D-glucopyranose (**9**; 18.0 g, 113.78 mmol), propane-1,3-dithiol (17.1 mL, 170.68 mmol), and boron trifluoride etherate (30 mL, 243 mmol) in dichloromethane (120 mL) was kept at 20° for 3 h, then cooled to −25°, and acetone (6 mL) and 2,2-dimethoxypropane (6 mL) were added. The mixture was kept for 30 min at 20°, then cooled to −25°, quenched with triethylamine (47 mL, 364 mmol) and saturated aq. sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Column chromatography (benzene–ether gradient 0→10%) of the residue yielded **13** (22 g, 63%), isolated as a syrup, $[\alpha]_D$ +4° (*c* 1). ^{1}H-N.m.r. data: δ 0.96 (d, 3 H, $J_{4,Me\text{-}4}$ 6.7 Hz, Me-4), 1.22 (d, 3 H, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 1.36 and 1.44 (2 s, 6 H, Me_2C), 1.98 (m, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 6.7 Hz, H-4), 2.05 (ddq, 1 H, $J_{2,3}$ 3, $J_{1,2}$ 4 Hz, H-2), 1.80–2.20 (m, 2 H, $SCH_2CH_2CH_2S$), 2.34 (bd, 1 H, $J_{HO,3}$ 4.5 Hz, HO-3), 2.80–3.00 (m, 4 H, $SCH_2CH_2CH_2S$), 3.75 (m, 1 H, $J_{5,6} = J_{6,6'}$ = 6 Hz, H-6), 3.94 (m, 1 H, H-3), 4.04 and 4.10 (m, 2 H, AB system H-5,6'), 4.15 (d, 1 H, H-1).

*2,4-Dideoxy-5,6-*O*-isopropylidene-3-*O*-(p-methoxybenzyl)-2,4-di-*C*-methyl-*D*-glucose trimethylene dithioacetal* (**14**). — A solution of **13** (22 g, 71.78 mmol) in dry *N*,*N*-dimethylformamide (130 mL) was stirred for 4 h at 20° with sodium hydride (4 g, 166.7 mmol), then *p*-methoxybenzyl chloride (11.7 mL, 86.29 mmol) was added, and stirring was continued for 15 h. The excess of sodium hydride was decomposed with methanol, the mixture was poured into water and extracted with ether, and the extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Column chromatography (benzene–ether gradient, 0→5%) of the residue yielded **14** (27.9 g, 91%), isolated as a syrup, $[\alpha]_D$ −3° (*c* 1). ^{1}H-N.m.r. data: δ 0.86 (d, 3 H, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 1.22 (d, 3 H, $J_{2,Me\text{-}2}$ 6.5 Hz, Me-2), 1.37 and 1.45 (2 s, 6 H, Me_2C), 1.85 (m, 1 H, H-2), 1.91 (ddq, 1 H, $J_{4,5}$ 3, $J_{3,4}$ 7.5 Hz, H-4), 2.10 (m, 2 H, $SCH_2CH_2CH_2S$), 2.80–2.95 (m, 4 H, $SCH_2CH_2CH_2S$), 3.69 (m, 1 H, $J_{6,6'} = J_{5,6}$ = 6 Hz, H-6), 3.80 (s, 3 H, MeO), 3.85 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-3), 4.05 (m, 2 H, AB system, H-5,6'), 4.08 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.56 and 4.63 (2 d, 2 H, J_{gem} 11 Hz, AB system, $MeOC_6H_4CH_2O$), 6.78–7.28 (2 m, 4 H, $MeOC_6H_4CH_2O$).

*2,4-Dideoxy-3-*O*-(p-methoxybenzyl)-2,4-di-*C*-methyl-*D*-glucose trimethylene dithioacetal* (**15**). — A solution of **14** (0.33 g, 0.723 mmol) in tetrahydrofuran (2 mL) and M

hydrochloric acid (2 mL) was kept for 80 h at 20°, then sodium hydrogen carbonate (pH > 7) was added, and the mixture was concentrated. The residue was poured into water and extracted with chloroform, and the extract was washed with saturated aq. sodium chloride, dried, and concentrated. Column chromatography (ethyl acetate) of the residue yielded **15** (0.26 g, 87%), isolated as a syrup, $[\alpha]_D$ +11° (*c* 1). ^{1}H-N.m.r. data: δ 0.89 (d, 3 H, $J_{4,Me-4}$ 7 Hz, Me-4), 1.27 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.85 (m, 1 H, $J_{3,4}$ 5 Hz, H-4), 2.05–2.20 (m, 3 H, $SCH_2CH_2CH_2S$, and H-2), 2.80–2.90 (m, 4 H, $SCH_2CH_2CH_2S$), 3.52 (dd, 1 H, $J_{5,6}$ 11, $J_{6,6'}$ 6 Hz, H-6), 3.62–3.78 (m, 2 H, AB system, H-5,6'), 3.80 (s, 3 H, MeO), 3.94 (dd, 1 H, $J_{2,3}$ 3 Hz, H-3), 4.05 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.61 (s, 2 H, $MeOC_6H_4CH_2O$), 6.85 and 7.29 (2 m, 4 H, $MeOC_6H_4CH_2O$).

*2,4-Dideoxy-3-*O-(p-*methoxybenzyl*)-*2,4-di*-C-*methyl*-L-xylo-*pentodialdose 5-(trimethylene dithioacetal)* (**16**). — A mixture of **15** (0.25 g, 0.647 mmol), potassium acetate (0.7 g), lead tetra-acetate (0.3 g, 0.679 mmol), and acetonitrile (6 mL) was stirred for 3 min at −25°, then diluted with ether, filtered through silica gel, and concentrated to yield **16** (0.198 g, 86%), m.p. 49–50°, $[\alpha]_D$ −3° (*c* 1). ^{1}H-N.m.r. data: δ 1.18 (d, 3 H, $J_{4,Me-4}$ 7 Hz, Me-4), 1.21 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.85 and 2.09 (2 m, 2 H, $SCH_2CH_2CH_2S$), 2.10 (ddq, 1 H, $J_{1,2}$ 5, $J_{2,3}$ 6 Hz, H-2), 2.77 (ddq, 1 H, $J_{3,4}$ 4, $J_{4,5}$ 1 Hz, H-4), 2.82–2.92 (m, 4 H, $SCH_2CH_2CH_2S$), 3.80 (s, 3 H, MeO), 4.06 (d, 1 H, H-1), 4.16 (dd, 1 H, H-3), 4.47 and 4.54 (2 d, 2 H, J_{gem} 11 Hz, AB system, $MeOC_6H_4CH_2O$), 6.87 and 7.25 (2 m, 4 H, $MeOC_6H_4CH_2O$), 9.82 (d, 1 H, H-5).

Anal. Calc. for $C_{18}H_{26}O_3S_2$: C, 60.98; H, 7.39. Found: C, 60.73; H, 7.28.

2,6-Di-tert-*butyl-4-methylphenyl 2,4,6-trideoxy-3-*O-(p-*methoxybenzyl*)-*2,4,6-tri*-C-*methyl*-L-glycero-L-ido-*hepturonate trimethylene dithioacetal* (**18**). — 0.88M Butyllithium in hexane (1.97 mL, 1.736 mmol) was added to a stirred solution of diisopropylamine (0.27 mL, 1.91 mmol) in dry tetrahydrofuran (3 mL) at −30°. The mixture was stirred for 30 min, then cooled to −70°, and a solution of 2,6-di-*tert*-butyl-4-methylphenyl propionate (**17**; 0.48 g, 1.736 mmol) in dry tetrahydrofuran (2.5 mL) was added. The mixture was stirred for 45 min, then cooled to −100°, and a solution of **16** (0.62 g, 1.75 mmol) in dry tetrahydrofuran (2.5 mL) was added. The mixture was stirred for 15 min, quenched at −100° with saturated aq. ammonium chloride, and extracted with ether. The extract was washed with water, saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 88:12) of the residue yielded **18** (0.991 g, 91%), isolated as a syrup, $[\alpha]_D$ +18° (*c* 1). ^{1}H-N.m.r. data: δ 1.12 (d, 3 H, $J_{4,Me-4}$ 7 Hz, Me-4), 1.17 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.33 and 1.35 (2 s, 18 H, 2 ^{t}Bu), 1.40 (d, 3 H, $J_{6,Me-6}$ 7.5 Hz, Me-6), 1.85 and 2.08 (2 m, 2 H, $SCH_2CH_2CH_2S$), 1.97 (m, 1 H, $J_{3,4} = J_{4,HO-5} = 2$ Hz, H-4), 2.22 (ddq, 1 H, $J_{2,3} = J_{1,2} = 8.5$ Hz, H-2), 2.34 (s, 3 H, MeC_6H_2), 2.72–2.92 (m, 4 H, $SCH_2CH_2CH_2S$), 2.88 (dq, 1 H, $J_{5,6}$ 9.5 Hz, H-6), 3.70 (dd, 1 H, $J_{5,HO-5}$ 2 Hz, HO-5), 3.82 (s, 3 H, MeO), 3.90 (ddd, 1 H, H-5), 4.02 (d, 1 H, H-1), 4.06 (dd, 1 H, H-3), 4.63 and 4.75 (2 d, 2 H, J_{gem} 11 Hz, AB system, $MeOC_6H_4CH_2O$), 6.88 and 7.32 (2 m, 4 H, $MeOC_6H_4CH_2O$), 7.14 (m, 2 H, MeC_6H_2).

2,6-Di-tert-*butyl-4-methylphenyl 2,4,6-trideoxy-3,5-*O-(S)-(p-*methoxybenzylidene*)-*2,4,6-tri*-C-*methyl*-L-glycero-L-ido-*hepturonate trimethylene dithioacetal* (**19**). — To a stirred solution of **18** (0.15 g, 0.238 mmol) in dry dichloromethane (3 mL) were added

powdered molecular sieves 3 Å (1 g) and 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ, 0.057 g, 0.25 mmol). The mixture was stirred for 3 min, quenched with saturated aq. sodium hydrogen carbonate, passed through a pad of Celite, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **19** (0.137 g, 92%), isolated as a syrup, $[\alpha]_D$ −2° (*c* 1). ^{1}H-N.m.r. data: δ 1.11 (d, 3 H, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 1.22 (d, 3 H, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 1.12 and 1.34 (2 s, 18 H, 2 ^{t}Bu), 1.43 (d, 3 H, $J_{6,Me\text{-}6}$ 7.5 Hz, Me-6), 1.89 (m, 1 H, H-4), 2.18 (m, 1 H, H-2), 1.90 and 2.13 (2 m, 2 H, $SCH_2CH_2CH_2S$), 2.79 (s, 3 H, MeC_6H_2), 2.83–2.93 (m, 4 H, $SCH_2CH_2CH_2S$), 3.01 (ddq, 1 H, $J_{5,6}$ 10 Hz, H-6), 3.80 (s, 3 H, MeO), 3.84 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 2 Hz, H-3), 4.25 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 4.27 (dd, 1 H, $J_{4,5}$ 2 Hz, H-5), 5.48 (s, 1 H, $MeOC_6H_4CH$), 6.83 and 7.36 (2 m, 4 H, $MeOC_6H_4CH$), 7.08 (m, 2 H, MeC_6H_2). N.O.e.: (H_{acetal}) H-3 8.3%, (H_{acetal}) H-5 7.1%.

*2,4,6-Trideoxy-3-*O-(p-*methoxybenzyl*)-*2,4,6-tri*-C-*methyl*-L-glycero-L-ido-*heptose trimethylene dithioacetal* (**21**). — A solution of **18** (0.815 g, 1.292 mmol) in dry tetrahydrofuran (3 mL) was added to a suspension of lithium aluminium hydride (0.245 g, 6.46 mmol) in dry tetrahydrofuran (3 mL). The mixture was stirred for 2 h, at 20°, then quenched with water (0.2 mL), followed by aq. 15% sodium hydroxide (0.2 mL), and water (0.6 mL). The mixture was then filtered through a pad of anhydrous sodium sulfate and concentrated. Chromatography (hexane–ethyl acetate, 1:1) of the residue yielded **21** (0.499 g, 96%), isolated as a syrup, $[\alpha]_D$ −6° (*c* 1).

*2,4,6-Trideoxy-5,7-*O-*isopropylidene-3-*O-(p-*methoxybenzyl*)-*2,4,6-tri*-C-*methyl*-L-glycero-L-ido-*heptose trimethylene dithioacetal* (**20**). — A mixture of **21** (0.012 g, 0.03 mmol), acetone (1 mL), 2,2-dimethoxypropane (0.5 mL), and toluene-*p*-sulfonic acid (5 mg) was kept for 10 min at 20°, then quenched with solid sodium hydrogen carbonate, concentrated, diluted with water, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **20** (0.013 g, 98%), isolated as a syrup, $[\alpha]_D$ −4° (*c* 1). ^{1}H-N.m.r. data: δ 0.69 (d, 3 H, $J_{6,Me\text{-}6}$ 7 Hz, Me-6), 1.06 (d, 3 H, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 1.12 (d, 3 H, $J_{2,Me\text{-}2}$ 7 Hz, Me-2), 1.41 and 1.47 (2 s, 6 H, Me_2C), 1.75–2.10 (m, 2 H, $SCH_2CH_2CH_2S$), 1.91 (m, 1 H, H-6), 1.95 (m, 1 H, H-4) 2.02 (m, 1 H, H-2), 2.68–2.90 (m, 4 H, $SCH_2CH_2CH_2S$), 3.45 (dd, 1 H, $J_{4,5}$ 2, $J_{5,6}$ 10.5 Hz, H-5), 3.51 (t, 1 H, $J_{6,7a} = J_{7a,7e}$ = 11.5 Hz, H-7*a*), 3.71 (dd, 1 H, $J_{6,7e}$ 5 Hz, H-7*e*), 3.81 (s, 3 H, MeO), 3.88 (dd, 1 H, $J_{2,3}$ 2, $J_{3,4}$ 8 Hz, H-3), 4.05 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.63 (s, 2 H, $MeOC_6H_4CH_2O$), 6.87 and 7.30 (2 m, 4 H, $MeOC_6H_4CH_2O$).

*2,4,6-Trideoxy-3-*O-(p-*methoxybenzyl*)-*2,4,6-tri*-C-*methyl-7-*S-*phenyl-7-thio*-L-glycero-L-ido-*heptose trimethylene dithioacetal* (**22**). — A solution of **21** (0.392 g, 0.974 mmol), diphenyl disulfide (0.319 g, 1.46 mmol), and tributyl phosphine (0.606 g, 2.434 mmol) in dry pyridine (3 mL) was kept under argon for 3 h at 20°, then diluted with water, and extracted with chloroform. The extract was washed with M hydrochloric acid, water, aq. 15% sodium hydroxide, and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 3:1) of the residue yielded **22** (0.452 g, 94%), isolated as a syrup, $[\alpha]_D$ −14° (*c* 1). ^{1}H-N.m.r. data: δ 0.95 (d, 3 H, $J_{4,Me\text{-}4}$ 7

Hz, Me-4), 0.99 (d, 3 H, $J_{6,Me-6}$ 7 Hz, Me-6), 1.22 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.80–2.00 (m, 4 H, $SCH_2CH_2CH_2S$, H-4,6), 2.17 (m, 1 H, H-2), 2.73 (d, 1 H, $J_{HO,5}$ 5.3 Hz, HO-5), 2.81 (dd, 1 H, $J_{6,7}$ 8.5, $J_{7,7'}$ 12.5 Hz, H-7), 2.81–2.92 (m, 4 H, $SCH_2CH_2CH_2S$), 3.46 (dd, 1 H, $J_{7',6}$ 3.5 Hz, H-7'), 3.54 (ddd, 1 H, $J_{4,5}$ 2, $J_{5,6}$ 9 Hz, H-5), 3.81 (dd, 1 H, $J_{2,3}$ 6.5 Hz, $J_{3,4}$ 4.4 Hz, H-3), 3.82 (s, 3 H, MeO), 4.06 (d, 1 H, H-1), 4.51 and 4.67 (2 d, 2 H, J_{gem} 11 Hz, AB system, $MeOC_6H_4CH_2O$), 6.88–7.32 (m, 9 H, PhS and $MeOC_6H_4CH_2O$).

*2,4,6-Trideoxy-3,5-*O-(S)-(p-*methoxybenzylidene*)-*2,4,6-tri-*C-*methyl-7-*S-*phenyl-7-thio-*L-glycero-L-ido-*heptose trimethylene dithioacetal* (**23**). — To a stirred solution of **22** (0.442 g, 0.893 mmol) in dry dichloromethane (7 mL) were added powdered molecular sieves 3 Å (2 g) and DDQ (0.213 g, 0.938 mmol). The mixture was stirred for 10 min, then quenched with saturated aq. sodium carbonate, passed through a pad of Celite, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 85:15) of the residue yielded **23** (0.379 g, 86%), isolated as a syrup, $[\alpha]_D$ −5° (*c* 1). ^{1}H-N.m.r. data: δ 0.96 (d, 3 H, $J_{4,Me-4}$ 7 Hz, Me-4), 1.06 (d, 3 H, $J_{6,Me-6}$ 7 Hz, Me-6), 1.25 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.85 (m, 3 H, $SCH_2CH_2CH_2S$ and H-4), 2.07–2.21 (m, 4 H, H-2,6 and $SCH_2CH_2CH_2S$), 2.84 (dd, 1 H, $J_{6,7}$ 8.5, $J_{7,7'}$ 13.5 Hz, H-7), 2.84–3.12 (m, 4 H, $SCH_2CH_2CH_2S$), 3.50 (dd, 1 H, $J_{7',6}$ 2.5 Hz, H-7'), 3.62 (dd, 1 H, $J_{4,5}$ 2, $J_{5,6}$ 10 Hz, H-5), 3.76 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 2 Hz, H-3), 3.82 (s, 3 H, MeO), 4.23 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.39 (s, 1 H, $MeOC_6H_4CH$), 6.85–7.45 (m, 9 H, PhS and $MeOC_6H_4CH$).

*1,2,3,5,7-Pentadeoxy-4,6-*O-(R)-(p-*methoxybenzylidene*)-*3,5,7-tri-*C-*methyl-8-*S-*phenyl-8-thio-*L-glycero-L-ido-*oct-1-enitol* (**24**). — A mixture of **23** (0.341 g, 0.692 mmol) and mercuric acetate (0.882 g, 2.768 mmol) in acetone (2.7 mL) and water (0.3 mL) was stirred for 20 h at 20°, then passed through silica gel with benzene–ethyl acetate (9:1), and concentrated. A solution of the residue in dry benzene (4 mL) was added to triphenylmethylenephosphorane prepared by the addition of 1.73M butyl-lithium in hexane (1.21 mL, 2.1 mmol) to a suspension of methyltriphenylphosphonium bromide (0.882 g, 2.3 mmol) in dry benzene (5 mL). The mixture was boiled for 10 min, the excess of phosphorane was decomposed with acetone, the precipitate was removed, and the filtrate was concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **24** (0.175 g, 63%), isolated as a syrup, $[\alpha]_D$ −20° (*c* 1). ^{1}H-N.m.r. data: δ 0.92 (d, 3 H, $J_{4,Me-4}$ 7 Hz, Me-4), 1.00 (d, 3 H, $J_{6,Me-6}$ 6.5 Hz, Me-6), 1.14 (d, 3 H, $J_{2,Me-2}$ 6.5 Hz, Me-2), 1.69 (t, 1 H, $J_{4,5} = J_{3,4}$ = 2 Hz, H-4), 2.11 (m, 1 H, H-6), 2.47 (m, 1 H, H-2), 2.87 (dd, 1 H, $J_{6,7}$ 8, $J_{7,7'}$ 13 Hz, H-7), 3.42 (dd, 1 H, $J_{2,3}$ 10 Hz, H-3), 3.47 (dd, 1 H, $J_{6,7'}$ 6.3 Hz, H-7'), 3.56 (dd, 1 H, $J_{5,6}$ 10 Hz, H-5), 3.83 (s, 3 H, MeO), 5.07 (dd, 1 H, $J_{1'cis,1}$ 10, $J_{1'cis,1'trans}$ 2 Hz, H-1'*cis*), 5.15 (ddd, 1 H, $J_{1'trans,1}$ 17, $J_{1'trans,2}$ 1 Hz, H-1'*trans*), 5.37 (s, 1 H, $MeOC_6H_4CH$), 5.65 (ddd, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 6.87–7.46 (m, 9 H, $MeOC_6H_4CH$ and PhS).

*1,2,3,5,7,8-Hexadeoxy-4,6-*O-(R)-(p-*methoxybenzylidene*)-*3,5,7-tri-*C-*methyl-8-*C-*phenylsulfonyl-*L-glycero-L-ido-*oct-1-enitol* (**6**). — A mixture of **24** (0.173 g, 0.432 mmol) and 85% *m*-chloroperbenzoic acid (0.175 g, 0.864 mmol) in dichloromethane (4 mL) was stirred for 5 min at 20°, then quenched with saturated aq. sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, passed through silica gel, and concentrated to yield **6**

(0.186 g, 99.6%) as a syrup, $[\alpha]_D$ −13° (*c* 0.5). ^{1}H-N.m.r. data: δ 0.84 (d, 3 H, $J_{4,Me\text{-}4}$ 7 Hz, Me-4), 1.09 (d, 3 H, $J_{2,Me\text{-}2}$ 6.5 Hz, Me-2), 1.15 (d, 3 H, $J_{6,Me\text{-}6}$ 7 Hz, Me-6), 1.70 (tq, 1 H, $J_{3,4} = J_{4,5} = 2$ Hz, H-4), 2.28 (m, 1 H, H-6), 2.42 (m, 1 H, H-2), 2.93 (dd, 1 H, $J_{6,7}$ 10, $J_{7,7'}$ 14 Hz, H-7), 3.35 (dd, 1 H, $J_{2,3}$ 10 Hz, H-3), 3.36 (dd, 1 H, $J_{6,7'}$ 2 Hz, H-7'), 3.66 (dd, 1 H, $J_{5,6}$ 14 Hz, H-5), 3.83 (s, 3 H, MeO), 5.06 (dd, 1 H, $J_{1'cis,1}$ 10, $J_{1'cis,1'trans}$ 2 Hz, H-1'*cis*), 5.13 (ddd, 1 H, $J_{1'trans,1}$ 17, $J_{1'trans,2}$ 1 Hz, H-1'*trans*), 5.31 (s, 1 H, $MeOC_6H_4CH$), 5.60 (ddd, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 6.75–7.80 (m, 9 H, $MeOC_6H_4CH$ and $PhSO_2$).

*2,4,6,8-Tetradeoxy-3-*O-(p-*methoxybenzyl*)-*2,4,6-tri-*C-*methyl-8,8,8-tri-*C-*phenyl-*L-glycero-D-gluco-*octos-7-ulose 1-(trimethylene dithioacetal)* (**26**). — To a stirred solution of ethyl trityl ketone (0.801 g, 2.666 mmol) in dry tetrahydrofuran (10 mL) was added 0.88M butyl-lithium in hexane (2.9 mL, 2.567 mmol). The mixture was stirred for 1 h at −78°, then cooled to −90°, and a solution of **16** (0.7 g, 1.975 mmol) in dry tetrahydrofuran (5 mL) was added. The mixture was stirred for an additional 15 min, then quenched with saturated aq. ammonium chloride at −90°, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ether, 3:1) of the residue yielded **26** (1.06 g, 82%), isolated as a syrup, $[\alpha]_D$ 0° (*c* 1). ^{1}H-N.m.r. data: δ 0.50 (d, 3 H, $J_{12,Me\text{-}12}$ 7 Hz, Me-12), 0.79 (d, 3 H, $J_{10,Me\text{-}10}$ 7 Hz, Me-10), 1.16 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.68 (m, 1 H, H-12), 1.75–2.12 (m, 2 H, $SCH_2CH_2CH_2S$), 3.18 (bd, 1 H, $J_{11,12}$ 10 Hz, H-11), 1.98 (m, 1 H, H-14), 2.75–2.95 (m, 4 H, $SCH_2CH_2CH_2S$), 3.20 (bq, 1 H, H-10), 3.56 (s, 1 H, HO-11), 3.80 (s, 3 H, MeO), 3.94 (dd, 1 H, $J_{12,13}$ 2, $J_{13,14}$ 8 Hz, H-13), 3.98 (d, 1 H, $J_{14,15}$ 3.5 Hz, H-15), 4.45 and 4.53 (2 d, 2 H, J_{gem} 11 Hz, AB system $MeOC_6H_4CH_2O$), 6.90–7.40 (m, 19 H, Tr and $MeOC_6H_4CH_2O$).

*2,4,6,8-Tetradeoxy-3,5-*O-(S)-(p-*methoxybenzylidene*)-*2,4,6-tri-*C-*methyl-8,8,8-tri-*C-*phenyl-*L-glycero-D-gluco-*octos-7-ulose 1-(trimethylene dithioacetal)* (**27**). — To a stirred solution of **26** (0.45 g, 0.687 mmol) in dry dichloromethane (4 mL) were added powdered molecular sieves 3 Å (2 g) and DDQ (0.164 g, 0.721 mmol). The mixture was stirred for 5 min, quenched with saturated aq. sodium hydrogen carbonate, passed through a pad of Celite, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **27** (0.44 g, 98%), isolated as a syrup, $[\alpha]_D$ −11° (*c* 1). ^{1}H-N.m.r. data: δ 0.95 (d, 3 H, $J_{10,Me\text{-}10}$ 6.6 Hz, Me-10), 1.17 (d, 3 H, $J_{14,Me\text{-}14}$ 6.5 Hz, Me-14), 1.25 (d, 3 H, $J_{12,Me\text{-}12}$ 7 Hz, Me-12), 1.70–2.10 (m, 2 H, $SCH_2CH_2CH_2S$), 2.06 (m, 1 H, H-14), 2.75–2.95 (m, 4 H, $SCH_2CH_2CH_2S$), 3.77 (dd, 1 H, $J_{12,13}$ 2, $J_{13,14}$ 10 Hz, H-13), 3.79 (s, 3 H, MeO), 3.83 (d, 1 H, $J_{14,15}$ 2.5 Hz, H-15), 4.12 (dq, 1 H, $J_{10,11}$ 10 Hz, H-10), 4.34 (d, 1 H, H-11), 5.20 (s, 1 H, $MeOC_6H_4CH$), 6.82–7.40 (m, 19 H, Tr and $MeOC_6H_4CH$). N.O.e.: (H_{acetal}) H-13 9%, (H_{acetal}) H-10 7.8%, (H_{acetal}) Me-10 3.4%.

*2,4,6,8-Tetradeoxy-3,5-*O-(R)-(p-*methoxybenzylidene*)-*2,4,6-tri-*C-*methyl-8,8,8-tri-*C-*phenyl-*L-glycero-D-gluco-*octos-7-ulose* (**28**). — A mixture of **27** (0.184 g, 0.282 mmol) and mercuric acetate (0.718 g, 2.25 mmol) in acetone (1.8 mL) and water (0.2 mL) was stirred for 22 h at 20°, then passed through silica gel with benzene–ethyl acetate (9:1), and concentrated to yield **28** (0.053 g, 33%) as a syrup, $[\alpha]_D$ −2° (*c* 1). ^{1}H-N.m.r.

data: δ 0.97 (d, 3 H, $J_{10,Me\text{-}10}$ 6.5 Hz, Me-10), 1.02 (d, 3 H, $J_{14,Me\text{-}14}$ 6.7 Hz, Me-14), 1.19 (d, 3 H, $J_{12,Me\text{-}12}$ 6.6 Hz, Me-12), 1.49 (m, 1 H, H-12), 2.57 (m, 1 H, H-14), 3.46 (dd, 1 H, $J_{12,13}$ 2.5, $J_{13,14}$ 9 Hz, H-13), 3.79 (s, 3 H, MeO), 4.14 and 4.25 (d and dq, 2 H, AB system, H-10,11), 5.25 (s, 1 H, $MeOC_6H_4CH$), 6.80–7.40 (m, 19 H, Tr and $MeOC_6H_4CH$), 9.36 (d, 1 H, $J_{14,15}$ 2.1 Hz, H-15).

*2,4-Dideoxy-5,6-*O*-isopropylidene-3-*O*-(*p*-methoxybenzyl)-2,4-di-*C*-methyl-*D*-glucose* (**29**). — A mixture of **14** (1.55 g, 3.633 mmol) and mercuric acetate (5.8 g, 18.2 mmol) in acetone (4 mL) and water (1 mL) was stirred for 26 h at 20°, then passed through silica gel with benzene–ethyl acetate (9:1), and concentrated to give **29** which was used in the next step without purification. A purified sample was a syrup, $[\alpha]_D$ −8° (*c* 1). ^{1}H-N.m.r. data: δ 0.84 (d, 3 H, $J_{12,Me\text{-}12}$ 6.7 Hz, Me-12), 1.17 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.36 and 1.40 (2 s, 6 H, Me_2C), 1.73 (m, 1 H, H-12), 2.76 (ddq, 1 H, $J_{14,15}$ 2, $J_{13,14}$ 7 Hz, H-14), 3.58 and 4.03 (2 m, 3 H, ABX system, H-10,10′,11), 3.82 (s, 3 H, MeO), 4.06 (dd, 1 H, $J_{12,13}$ 3 Hz, H-13), 4.58 (s, 2 H, $MeOC_6H_4CH_2O$), 6.89 and 7.28 (2 m, 4 H, $MeOC_6H_4CH_2O$), 9.79 (d, 1 H, H-15).

*3,5,7-Trideoxy-1,2-*O*-isopropylidene-4-*O*-(*p*-methoxybenzyl)-3,5,7-tri-*C*-methyl-*L*-glycero-*L*-gulo-heptitol* (**30**). To a stirred suspension of copper(I) bromide dimethyl sulfide complex (1.088 g, 5.29 mmol) in dry ether (10 mL) was added 1.19M methyl-lithium in ether (8.89 mL, 10.58 mmol) at −40°. The mixture was stirred for 10 min at −40°, then cooled to −78°, and a solution of **29** in dry ether (5 mL) was added. The mixture was stirred for 10 min, quenched with saturated aq. ammonium chloride, and extracted with ether. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 2:1) of the residue yielded **30** (0.499 g, 39%), isolated as a syrup, $[\alpha]_D$ −20° (*c* 1). ^{1}H-N.m.r. data: δ 0.90 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 0.95 (d, 3 H, $J_{12,Me\text{-}12}$ 6.6 Hz, Me-12), 1.17 (d, 3 H, $J_{15,Me\text{-}15}$ 6 Hz, Me-15), 1.34 and 1.39 (2 s, 6 H, Me_2C), 1.82 (m, 1 H, H-12), 1.96 (m, 1 H, H-14), 3.36 (bs, 1 H, HO-15), 3.56 (t, 1 H, $J_{10,10'} = J_{10,11} = 7.2$ Hz, H-10), 3.81 (s, 3 H, MeO), 3.81 (dd, 1 H, $J_{13,14}$ 5.5, $J_{12,13}$ 2.5 Hz, H-13), 3.86 (bdq, 1 H, $J_{14,15}$ 1.5 Hz, H-15), 3.96 and 3.99 (2 m, 2 H, AB system, H-10′,11), 4.48 and 4.67 (2 d, 2 H, J_{gem} 11 Hz, AB system, $MeOC_6H_4CH_2O$), 6.87 and 7.28 (2 m, 4 H, $MeOC_6H_4CH_2O$).

*3,5,7-Trideoxy-1,2:4,6-di-*O*-isopropylidene-3,5-di-*C*-methyl-*L*-glycero-*L*-gulo-heptitol* (**31**). — A mixture of **30** (0.032 g, 0.09 mmol), Raney nickel (1 g), and methanol (3 mL) was boiled for 2 h, filtered, and concentrated. A mixture of the residue, acetone (1 mL), 2,2-dimethoxypropane (0.5 mL), and toluene-*p*-sulfonic acid (50 mg) was kept for 15 min at 20°, then quenched with saturated aq. sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **31** (0.02 g, 82%), isolated as a syrup, $[\alpha]_D$ −15° (*c* 1). ^{1}H-N.m.r. data: δ 0.90 (d, 3 H, $J_{12,Me\text{-}12}$ 6.4 Hz, Me-12), 0.95 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.22 (d, 3 H, $J_{15,Me\text{-}15}$ 7 Hz, Me-15), 1.33, 1.35, and 1.41 (3 s, 12 H, 2 Me_2C), 1.68 (m, 1 H, H-14), 1.99 (m, 1 H, H-12), 3.40 (dq, 1 H, $J_{14,15}$ 8 Hz, H-15), 3.59 (dd, 1 H, $J_{13,14}$ 4.5, $J_{12,13}$ 8.6 Hz, H-13), 3.64 (m, 1 H, H-10), 3.94 (m, 2 H, AB system, H-10,11).

6-O-Benzyl-3,5,7-trideoxy-1,2-O-isopropylidene-4-O-(p-methoxybenzyl)-3,5-di-C-methyl-L-glycero-L-gulo-heptitol (**32**). — A solution of **30** (0.387 g, 1.098 mmol) in dry *N,N*-dimethylformamide (5 mL) was stirred for 30 min at 20° with sodium hydride (0.053 g, 2.2 mmol) then benzyl bromide (0.17 mL, 1.42 mmol) was added, and stirring was continued for 30 min. The excess of sodium hydride was decomposed with methanol, and the mixture was poured into water and extracted with ether. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 4:1) of the residue yielded **32** (0.471 g, 97%), isolated as a syrup, $[\alpha]_D$ −10° (*c* 1). ^{1}H-N.m.r. data: δ 0.82 (d, 3 H, $J_{12,Me\text{-}12}$ 7.2 Hz, Me-12), 1.08 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.16 (d, 3 H, $J_{15,Me\text{-}15}$ 6.5 Hz, Me-15), 1.39 and 1.42 (2 s, 6 H, Me_2C), 1.69 (m, 1 H, H-12), 2.10 (m, 1 H, H-14), 3.49 (dq, 1 H, $J_{14,15}$ 5.5 Hz, H-15), 3.59 (m, 1 H, H-10), 3.69 (dd, 1 H, $J_{12,13}$ 3, $J_{13,14}$ 8 Hz, H-13), 3.82 (s, 3 H, MeO), 4.06 and 4.09 (2 m, 2 H, AB system, H-10,11), 4.48 and 4.54, 4.53 and 4.59 (4 d, 4 H, 2 AB systems, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$), 6.89 and 7.30 (2 m, 9 H, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$).

6-O-Benzyl-3,5,7-trideoxy-4-O-(p-methoxybenzyl)-3,5-di-C-methyl-L-glycero-L-gulo-heptitol (**33**). — A solution of **32** (0.06 g, 0.136 mmol) in tetrahydrofuran (1 mL) and M hydrochloric acid (1 mL) was kept for 60 h at 20°, then sodium hydrogen carbonate was added, and the mixture was concentrated. The residue was diluted with water and extracted with chloroform, and the extract was washed with saturated aq. sodium chloride, dried, and concentrated. Chromatography (ethyl acetate) of the residue yielded **33** (0.049 g, 90%), isolated as a syrup, $[\alpha]_D$ +39° (*c* 1). ^{1}H-N.m.r. data: δ 0.85 (d, 3 H, $J_{12,Me\text{-}12}$ 6.7 Hz, Me-12), 1.06 (d, 3 H, $J_{14,Me\text{-}14}$ 6.5 Hz, Me-14), 1.17 (d, 3 H, $J_{15,Me\text{-}15}$ 6 Hz, Me-15), 1.88 (ddq, 1 H, $J_{14,15}$ 6, $J_{13,14}$ 3.5 Hz, H-14), 2.05 (m, 1 H, $J_{11,12}$ 6.7, $J_{12,13}$ 3.5 Hz, H-12), 2.15 and 3.96 (2 m, 2 H, HO-9,10), 3.34 (dq, 1 H, H-15), 3.48 (m, 1 H, H-10), 3.70 (m, 2 H, AB system, H-10,11), 3.79 (s, 3 H, MeO), 3.83 (t, 1 H, H-13), 4.30 and 4.54 (2 m, 4 H, 2 AB systems, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$), 6.85–7.40 (m, 9 H, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$).

8-O-Benzyl-1,3,5,7,9-pentadeoxy-6-O-(p-methoxybenzyl)-3,5,7-tri-C-methyl-1,1,1-tri-C-phenyl-L-erythro-D-galacto-non-2-ulose (**35**). — A mixture of **33** (0.281 g, 0.698 mmol), potassium acetate (0.9 g), lead tetra-acetate (0.325 g, 0.733 mmol), and acetonitrile (2 mL) was stirred for 1 min at −25°, then diluted with ether, filtered through silica gel, and concentrated to yield pure **34**. To a solution of ethyl trityl ketone (0.419 g, 1.396 mmol) in dry tetrahydrofuran (5 mL) was added 1.73M butyl-lithium in hexane (0.726 mL, 1.256 mmol) at −60°, the mixture was stirred for 1 h, then cooled to −90°, and a solution of **34** in dry tetrahydrofuran (2 mL) was added. The mixture was stirred for 20 min at −90°, quenched with saturated aq. ammonium chloride, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 4:1) of the residue yielded **35** (0.411 g, 88%), isolated as a syrup, $[\alpha]_D$ +4° (*c* 1). ^{1}H-N.m.r. data: δ 0.43 (d, 3 H, $J_{12,Me\text{-}12}$ 7 Hz, Me-12), 0.72 (d, 3 H, $J_{10,Me\text{-}10}$ 7 Hz, Me-10), 0.96 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.07 (d, 3 H, $J_{15,Me\text{-}15}$ 6.5 Hz, Me-15), 1.43 (m, 1 H, H-12), 1.93 (m, 1 H, H-14), 3.14 (d, 1 H, $J_{11,12}$ 10 Hz, H-11), 3.16 (q, 1 H, H-10), 3.33 (dq, 1 H, $J_{14,15}$ 5.5 Hz, H-15),

3.52 (bs, 1 H, HO-11), 3.69 (dd, 1 H, $J_{12,13}$ 2, $J_{13,14}$ 8 Hz, H-13), 3.79 (s, 3 H, MeO), 4.42 (m, 4 H, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$), 6.88–7.40 (m, 24 H, $MeOC_6H_4CH_2O$, $C_6H_5CH_2O$, and Tr).

*8-O-Benzyl-1,3,5,7,9-pentadeoxy-4,6-O-(R)-(p-methoxybenzylidene)-3,5,7-tri-C-methyl-1,1,1-tri-C-phenyl-*L-erythro-D-galacto-*non-2-ulose* (**36**). — To a stirred solution of **35** (0.391 g, 0.583 mmol) in dry dichloromethane (5 mL) were added powdered molecular sieves 3 Å (2 g) and DDQ (0.139 g, 0.612 mmol). The mixture was stirred for 5 min, quenched with saturated aq. sodium hydrogen carbonate, passed through a pad of Celite, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ether, 4:1) of the residue yielded **36** (0.285 g, 73%), isolated as a syrup, $[\alpha]_D$ −2° (*c* 1). ^{1}H-N.m.r. data: δ 0.50 (d, 3 H, $J_{15,Me-15}$ 6.5 Hz, Me-15), 0.85 (d, 3 H, $J_{10,Me-10}$ 6.5 Hz, Me-10), 0.88 (d, 3 H, $J_{12,Me-12}$ 7.5 Hz, Me-12), 0.97 (d, 3 H, $J_{14,Me-14}$ 6.5 Hz, Me-14), 1.28 (m, 1 H, H-12), 2.16 (m, 1 H, H-14), 3.16 (dq, 1 H, $J_{14,15}$ 3.5 Hz, H-15), 3.31 (dd, 1 H, $J_{13,14}$ 10, $J_{12,13}$ 2 Hz, H-13), 3.79 (s, 3 H, MeO), 4.14 and 4.25 (dq and d, 2 H, AB system, H-10,11), 4.41 and 4.50 (2 d, 2 H, J_{gem} 12 Hz, AB system, $C_6H_5CH_2O$), 5.24 (s, 1 H, $MeOC_6H_4CH$), 6.83–7.43 (m, 24 H, $MeOC_6H_4CH$, $C_6H_5CH_2O$, and Tr). N.O.e.: (H_{acetal}) H-13 9.3%, (H_{acetal}) H-10 8.4%.

*7-O-Benzyl-2,4,6,8-tetradeoxy-3,5-O-(S)-(p-methoxybenzylidene)-2,4,6-tri-C-methyl-*L-erythro-D-galacto-*octitol* (**37**). — A mixture of **36** (0.265 g, 0.396 mmol) and M lithium triethylborohydride in tetrahydrofuran (2.5 mL, 2.5 mmol) was kept under argon for 80 h at 20°, then quenched with aq. 15% sodium hydroxide (2.3 mL) and aq. 30% hydrogen peroxide (2.3 mL). The mixture was stirred for 2 h at 20°, then extracted with chloroform, and the extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 1:1) of the residue yielded **37** (0.157 g, 93%), m.p. 130–131° (from pentane–ethyl acetate), $[\alpha]_D$ +5.7° (*c* 1). ^{1}H-N.m.r. data: δ 1.05 (d, 3 H, $J_{14,Me-14}$ 7 Hz, Me-14), 1.09 (d, 3 H, $J_{10,Me-10}$ 7 Hz, Me-10), 1.12 (d, 3 H, $J_{15,Me-15}$ 6.5 Hz, Me-15), 1.19 (d, 3 H, $J_{12,Me-12}$ 7 Hz, Me-12), 1.81 (tq, 1 H, $J_{12,13}$ 2.2, $J_{11,12}$ 1 Hz, H-12), 2.20 (ddq, 1 H, $J_{13,14}$ 9, $J_{14,15}$ 4.5 Hz, H-14), 2.47 (m, 1 H, H-10), 3.54 (dd, 1 H, $J_{10,11}$ 10 Hz, H-11), 3.56 (bs, 2 H, H-9,9'), 3.59 (dq, 1 H, H-15), 3.78 (dd, 1 H, H-13), 3.81 (s, 3 H, MeO), 4.50 and 4.56 (2 d, 2 H, J_{gem} 12 Hz, AB system, $C_6H_5CH_2O$), 5.66 (s, 1 H, $MeOC_6H_4CH$), 6.90–7.48 (m, 9 H, $MeOC_6H_4CH$ and $C_6H_5CH_2O$).

Anal. Calc. for $C_{26}H_{36}O_5$: C, 72.86; H, 8.47. Found: C, 72.73; H, 8.32.

*10-O-Benzyl-1,2,3,5,7,9,11-heptadeoxy-6,8-O-(R)-(p-methoxybenzylidene)-2,5,7,9-tetra-C-methyl-*L-arabino-L-gluco-*undec-2-enitol* (**39**). — A solution of methyl sulfoxide (0.035 mL, 0.493 mmol) in dry dichloromethane (0.3 mL) was added during 5 min at −60° to a solution of oxalyl chloride (0.03 mL, 0.349 mmol) in dry dichloromethane (0.6 mL). The mixture was stirred for 10 min, a solution of **37** (0.07 g, 0.163 mmol) in dry dichloromethane (0.6 mL) was added, and stirring was continued for 15 min at −60°. Triethylamine (0.16 mL, 1.148 mmol) was added, the temperature of the mixture was rapidly elevated to 0°, M hydrochloric acid (10 mL) was added, and the aqueous layer was extracted with chloroform. The extract was washed with water, saturated aq. sodium hydrogen carbonate, and saturated aq. sodium chloride, dried, and concentrated. The residue was the pure aldehyde **38** (0.069 g).

1.2M *tert*-Butyl-lithium in pentane (1.63 mL, 1.96 mmol) was added to a solution of isobutenyl bromide (0.132 g, 0.98 mmol) in dry tetrahydrofuran (2.8 mL), ether (0.7 mL), and pentane (0.7 mL) at −120°. The mixture was stirred for 1 h at −120 to −110° then dry ether (2 mL) and copper(I) bromide–dimethyl sulfide complex (0.1 g, 0.49 mmol) were added. The mixture was warmed to −50°, stirred at −50° for 10 min, and cooled to −78°, and a solution of **38** (0.069 g, 0.163 mmol) in dry ether (1.5 mL) was added. The mixture was stirred for 10 min at −78°, quenched with saturated aq. ammonium chloride, and extracted with ether. The extract was washed with water, saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 4:1) of the residue yielded **39** (0.063 g, 80%), isolated as a syrup, $[\alpha]_D$ −0.5° (*c* 1). ^{1}H-N.m.r. data: δ 1.05 (d, 6 H, $J_{10,Me\text{-}10} = J_{14,Me\text{-}14}$ 7 Hz, Me-10,14), 1.12 (d, 3 H, $J_{15,Me\text{-}15}$ 6.4 Hz, Me-15), 1.20 (d, 3 H, $J_{12,Me\text{-}12}$ 6.8 Hz, Me-12), 1.65 and 1.74 (2 d, 6 H, $J_{8,Me\text{-}7}$ 1 Hz, 2 Me-7), 1.93 (m, 1 H, H-12), 2.24 (m, 1 H, H-14), 2.37 (m, 1 H, H-10), 3.62 (dq, 1 H, $J_{14,15}$ 4 Hz, H-15), 3.72 (dd, 1 H, $J_{11,12}$ 1.2, $J_{10,11}$ 10.5 Hz, H-11), 3.74 (dd, 1 H, $J_{12,13}$ 2, $J_{13,14}$ 9.5 Hz, H-13), 3.81 (s, 3 H, MeO), 4.41 (dd, 1 H, $J_{9,10}$ 3, $J_{8,9}$ 8.8 Hz, H-9), 4.50 and 4.57 (2 d, 2 H, J_{gem} 11.5 Hz, AB system, $C_6H_5CH_2O$), 5.27 (m, 1 H, H-8), 5.62 (s, 1 H, $MeOC_6H_4CH$), 6.85–7.45 (m, 9 H, $MeOC_6H_4CH$ and $C_6H_5CH_2O$).

10-O-*Benzyl-1,2,3,5,7,9,11-heptadeoxy-4*-O-(p-*methoxybenzyl*)-*6,8*-O-(R)-(p-*methoxybenzylidene*)-*2,5,7,9-tetra*-C-*methyl*-L-arabino-L-gluco-*undec-2-enitol* (**40**). — A solution of **39** (0.053 g, 0.11 mmol) in dry *N,N*-dimethylformamide (2 mL) was stirred for 30 min at 20° with sodium hydride (0.012 g, 0.5 mmol), then *p*-methoxybenzyl chloride (0.018 mL, 0.132 mmol) was added, and stirring was continued for 1 h. The excess of sodium hydride was decomposed with methanol, the mixture was poured into water, and then extracted with ether. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 9:1) of the residue yielded **40** (0.065 g, 98%), isolated as a syrup, $[\alpha]_D$ −32° (*c* 1). ^{1}H-N.m.r. data: δ 0.91, 1.00, 1.05, and 1.13 (4 d, 12 H, *J* 6.5 Hz, Me-10,12,14,15), 1.60 (m, 1 H, H-12), 1.60 and 1.82 (2 bs, 6 H, 2 Me-7), 2.18 (m, 1 H, H-14), 2.43 (m, 1 H, H-10), 3.35 (dq, 1 H, $J_{14,15}$ 3.5 Hz, H-15), 3.60 (dd, 1 H, $J_{12,13}$ 2, $J_{13,14}$ 9.8 Hz, H-13), 3.75 (d, 1 H, $J_{10,11}$ 11 Hz, H-11), 3.80 (s, 6 H, 2 MeO), 3.99 (dd, 1 H, $J_{9,10}$ 3 Hz, H-9), 4.13 and 4.49 (2 d, 2 H, J_{gem} 11.5 Hz, AB system, $MeOC_6H_4CH_2O$), 4.42 and 4.52 (2 d, 2 H, J_{gem} 11 Hz, AB system, $C_6H_5CH_2O$), 5.22 (bd, 1 H, H-8), 5.57 (s, 1 H, $MeOC_6H_4CH$), 6.85–7.45 (m, 13 H, $MeOC_6H_4CH$, $MeOC_6H_4CH_2O$, and $C_6H_5CH_2O$).

10-O-*Benzyl-1,2,3,5,7,9,11-heptadeoxy-4*-O-(p-*methoxybenzyl*)-*2,5,7,9-tetra*-C-*methyl*-L-arabino-L-gluco-*undec-2-enitol* (**41**). — A solution of **40** (0.06 g, 0.099 mmol) in tetrahydrofuran (1 mL) and M hydrochloric acid (1 mL) was kept for 1 h at 20°, then sodium hydrogencarbonate was added, and the mixture was concentrated. The residue was diluted with water and extracted with chloroform. The extract was washed with saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 2:1) of the residue yielded **40** (0.023 g, 38%), and **41** (0.026 g, 55%; 89% with respect to **40** consumed), isolated as a syrup, $[\alpha]_D$ −25° (*c* 1). ^{1}H-N.m.r. data: δ 0.75 (d, 3 H, $J_{12,Me\text{-}12}$ 7 Hz, Me-12), 0.97 (d, 3 H, $J_{10,Me\text{-}10}$ 7 Hz, Me-10), 1.05 (d, 3 H, $J_{14,Me\text{-}14}$ 7 Hz, Me-14), 1.16 (d, 3 H, $J_{15,Me\text{-}15}$ 6.5 Hz, Me-15), 1.62 (m, 1 H, H-10), 1.72 (m, 1 H,

H-12), 1.64 and 1.80 (2 d, 6 H, 2 Me-7), 1.93 (m, 1 H, H-14), 3.52 (dq, 1 H, $J_{14,15}$ 4.5 Hz, H-15), 3.72 (dd, 1 H, $J_{11,12}$ 9, $J_{10,11}$ 1.5 Hz, H-11), 3.81 (s, 3 H, MeO), 3.92 (dd, 1 H, $J_{13,14}$ 5, $J_{12,13}$ 3 Hz, H-13), 4.22 (dd, 1 H, $J_{8,9}$ 9.5, $J_{9,10}$ 4 Hz, H-9), 4.22 and 4.51, 4.45 and 4.56 (4 d, 4 H, 2 AB systems, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$), 5.23 (m, 1 H, H-8), 6.80–7.40 (m, 9 H, $MeOC_6H_4CH_2O$ and $C_6H_5CH_2O$).

*10-O-Benzyl-1,2,3,5,7,9,11-heptadeoxy-4,6-O-(R)-(p-methoxybenzylidene)-2,5,7,9-tetra-C-methyl-*L-arabino-L-gluco-*undec-2-enitol* (**42**). — To a stirred solution of **41** (0.017 g, 0.036 mmol) in dry dichloromethane (1 mL) were added powdered molecular sieves 3 Å (0.2 g) and DDQ (9 mg, 0.039 mmol). The mixture was stirred for 3 min, quenched with saturated aq. sodium hydrogencarbonate, passed through a pad of Celite, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 7:3) of the residue yielded **42** (0.014 g, 83%), isolated as a syrup, $[\alpha]_D$ +18° (*c* 0.5). ^{1}H-N.m.r. data: δ 0.84 (d, 3 H, $J_{12,Me-12}$ 7 Hz, Me-12), 1.01 (d, 3 H, $J_{14,Me-14}$ 7 Hz, Me-14), 1.02 (d, 3 H, $J_{10,Me-10}$ 7 Hz, Me-10), 1.15 (d, 3 H, $J_{15,Me-15}$ 6.5 Hz, Me-15), 1.57 (m, 1 H, H-10), 1.71 and 1.75 (2 d, 6 H, $J_{8,Me-7}$ 1.5 Hz, 2 Me-7), 1.89 (m, 1 H, H-12), 1.95 (m, 1 H, H-14), 2.57 (m, 1 H, HO-13), 3.54 (dq, 1 H, $J_{14,15}$ 5 Hz, H-15), 3.80 (s, 3 H, MeO), 3.82 (dq, 1 H, $J_{10,11}$ 2, $J_{11,12}$ 10 Hz, H-11), 3.96 (m, 1 H, H-13), 4.43 and 4.58 (2 d, 2 H, J_{gem} 11.5 Hz, AB system, $C_6H_5CH_2O$), 4.61 (dd, 1 H, $J_{8,9}$ 8, $J_{9,10}$ 2.1 Hz, H-9), 5.35 (m, 1 H, H-8), 5.55 (s, 1 H, $MeOC_6H_4CH$), 6.80–7.40 (m, 9 H, $MeOC_6H_4CH$ and $C_6H_5CH_2O$).

*10-O-Benzyl-1,2,3,5,7,9,11-heptadeoxy-6,8-O-(p-methoxybenzylidene)-2,5,7,9-tetra-C-methyl-*L-arabino-L-manno-*undec-2-enitol* (**43**). — A solution of **39** (0.0105 g, 0.0218 mmol), triphenylphosphine (0.023 g, 0.087 mmol), benzoic acid (0.008 g, 0.065 mmol), and diethyl azodicarboxylate (0.01 g, 0.065 mmol) in tetrahydrofuran (1 mL) was kept for 2 h at 20°, then quenched with water, and extracted with chloroform. The extract was washed with water, concentrated, diluted with methanol (1 mL) and aq. 15% sodium hydroxide (0.1 mL), heated for 3 h at 60°, then concentrated, diluted with water, and extracted with chloroform. The extract was washed with water and saturated aq. sodium chloride, dried, and concentrated. Chromatography (hexane–ethyl acetate, 4:1) of the residue yielded **43** (0.009 g, 85%), isolated as a syrup $[\alpha]_D$ +12° (*c* 0.5). ^{1}H-N.m.r. data: δ 1.01 (d, 3 H, $J_{10,Me-10}$ 7 Hz, Me-10), 1.05 (d, 3 H, $J_{14,Me-14}$ 7 Hz, Me-14), 1.14 (d, 3 H, $J_{12,Me-12}$ 6.5 Hz, Me-12), 1.15 (d, 3 H, $J_{15,Me-15}$ 6.5 Hz, Me-15), 1.63 and 1.73 (2 d, 6 H, $J_{8,Me-7}$ 1.5 Hz, 2 Me-7), 1.84 (m, 1 H, H-12), 2.20 (m, 1 H, H-14), 2.48 (m, 1 H, H-10), 3.45 (dd, 1 H, $J_{10,11}$ 10, $J_{11,12}$ 1.5 Hz, H-11), 3.58 (dq, 1 H, $J_{15,14}$ 4.5 Hz, H-15), 3.81 (s, 3 H, MeO), 3.82 (dd, 1 H, $J_{12,13}$ 2.5, $J_{13,14}$ 9.5 Hz, H-13), 4.26 (m, 1 H, H-9), 4.50 and 4.56 (2 d, 2 H, J_{gem} 11.5 Hz, AB system, $C_6H_5CH_2O$), 5.20 (m, 1 H, $J_{8,9}$ 9.5 Hz, H-8), 5.63 (s, 1 H, $MeOC_6H_4CH$), 685–7.45 (m, 9 H, $MeOC_6H_4CH$ and $C_6H_5CH_2O$).

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