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A SYNTHETIC APPROACH TO OLGUINE: A MODEL STUDY

ROSA Mª. RABANAL, JAVIER ESCUDERO, MANUEL MARTIN-LOMAS, SERAFIN VALVERDE*,
Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)

AUREA PERALES, AND JOSE FAYOS
Instituto Rocasolano, CSIC, Serrano 119, 28006 Madrid (Spain)
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ABSTRACT

A model study for a synthetic approach to the α,β-unsaturated δ-lactone olguine is reported starting from 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose by Wittig reaction with (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide and epoxidation of the resulting olefins. The crystal and molecular structures of the intermediate epoxide 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-α-L-*erythro*-D-*galacto*-octopyranose have been determined.

INTRODUCTION

A large number of natural products contain α,β-unsaturated lactone structures[1] and their synthesis can be envisaged from carbohydrate precursors[2]. The α,β-unsaturated-δ-lactones olguine (**1**) and anamarine (**2**) have been isolated from an unclassified *Hyptis* species[3,4]. The preparation of sugars with an extended chain has attracted considerable attention[5] and we now report some aspects of the synthesis of the side-chain of **1** which could also be applied to the side-chain of asperlin (**3**). The enantiomer of **3** has been synthesised from D-galactose[6]. This synthesis demonstrated the *trans* configuration of the epoxypropyl group, although the stereochemistry of the epoxide ring was not determined.

RESULTS AND DISCUSSION

Condensation of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**4**) with (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide[7] gave a mixture (46%) of the olefins **5** and **6** (3:7 ratio). These products were isolated but not further characterised. Treatment of the mixture of **5** and **6** with hydrochloric acid in tetrahydrofuran gave the *trans*-aldehyde (**7**, 90%), the ^{1}H-n.m.r. spectrum of which showed signals for the aldehyde proton at δ 9.6 and for the olefinic protons

*To whom enquiries should be addressed.

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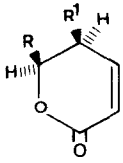
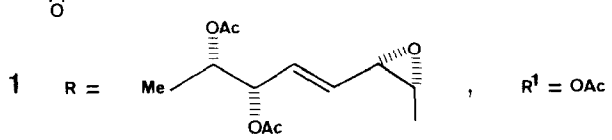
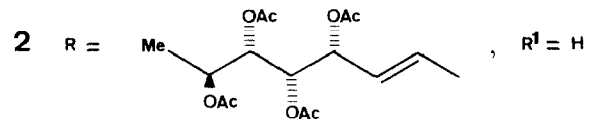
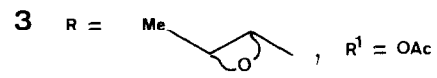


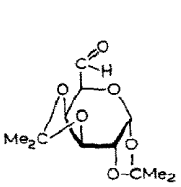






at δ 6.80 and 6.35 (J 15.3 Hz). Reduction of **7** with sodium borohydride in methanol at 0° afforded the alcohol **8**. Mesylation of **8** at −20° proceeded normally (t.l.c.), but attempts to isolate the mesylate failed. Consequently, **8** was mesylated and the product was treated with $LiAlH_4$, without isolation, to give **9** (66%). Reaction of **9** with *m*-chloroperbenzoic acid yielded a mixture of the epoxides **10** and **11** in the ratio 1:4. The configurations of **10** and **11** were assigned tentatively on the basis of ^{13}C-n.m.r. data. For **10**, there was a significant difference between the chemical shifts of the signals for C-6 and C-7 which was not observed for **11**, possibly because of the steric interaction of C-7 with the 4-substituent in **10**.

Treatment of **6** with silica gel–oxalic acid gave the *cis*-aldehyde **12**, the ^{1}H-n.m.r. spectrum of which contained a signal for an aldehyde proton at δ 10.1 and for olefinic protons at δ 6.55 and 6.10 (J 12 Hz). Attempted epoxidation of **12** with hydrogen peroxide failed to give the corresponding epoxyaldehyde. Reduction of **12** with sodium borohydride in methanol at 0° afforded the *cis*-alcohol **13** which, on treatment with *m*-chloroperbenzoic acid, gave a mixture of the epoxides **14** and **15** in the ratio 1:3. The crystal structure of **15** is shown in Fig. 1. The orientation of the epoxide ring with respect to the pyranoid ring is such that H-5 and H-6 are almost *trans*, the angle H-5–C-5–C-6–H-6 being 173.4 (3)°. The epoxide oxygen is oriented towards the pyranose ring oxygen, as shown by the value[6] of −160.2 (3)° for the angle C-4–C-5–C-6–O-6. There is an intermolecular hydrogen-bond O-8–H---O-6 of 2.881 (4) Å. Cremer conformational analysis[8] of rings A–C has been done by beginning the rotation clockwise at O-5, O-2, and O-3 in Fig. 1. The results are: ϕ 2A = 34.0 (3)°, ϕ 2B = 179.4 (5)°, ϕ 2C = 4.3 (8)°, θ 2A = 80.4 (3)°, QA = 0.644 (3), QB = 0.321 (3), and QC 0.271 (3) Å. Thus, looking at the molecule as in Fig. 1, ring A is a twist $^{01}T_{C2}$, and the five membered rings B and C



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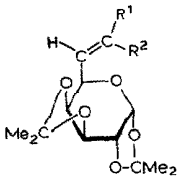


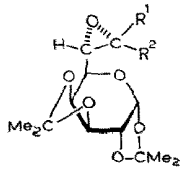
5 R^1 =  , R^2 = H, **12** R^1 = H, R^2 =

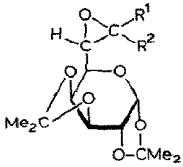
6 R^1 = H, R^2 =  ; **13** R^1 = H, R^2 = CH_2OH

7 R^1 =  , R^2 = H

8 R^1 = CH_2OH, R^2 = H

9 R^1 = CH_3, R^2 = H





10 R^1 = CH_3, R^2 = H, **11** R^1 = CH_3, R^2 = H

14 R^1 = H, R^2 = CH_2OH; **15** R^1 = H, R^2 = CH_2OH

16 R^1 = H, R^2 =  , **17** R^1 = H, R^2 = 

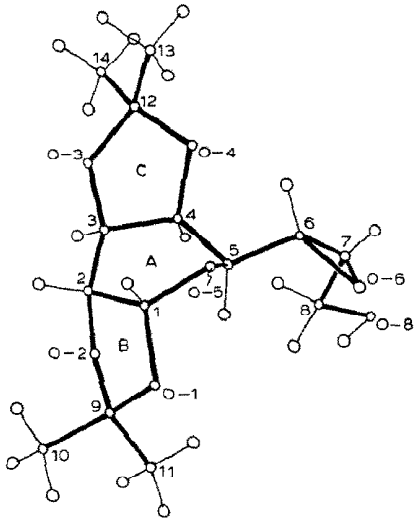


Fig.1. X-Ray structure of 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-α-L-*erythro*-D-*galacto*-octopyranose (**15**).

are envelopes E_{03} and ^{04}E, respectively. In the substituent at C-5, C-5–C-6–C-8–O-8 are almost coplanar, the torsion at C-6–C-7 being 2.6 (5)° and that at C-7–C-8 −174.7 (3)°. The 360-MHz n.m.r. data for **12** indicated that the six-membered ring has a skew-boat conformation, as previously reported for 1,2:3,4-di-*O*-isopropylidene-D-galactose derivatives[9]; the couplings $J_{1,2}$ 5.0, $J_{2,3}$ 2.5, $J_{3,4}$ 7.5, and $J_{4,5}$ 2.0 Hz are almost identical to those reported[9]. This conformation is similar to that of **15** in the crystalline solid.

The β configuration of the epoxide ring of this major reaction product accords with the previous configurational assignment of the major epoxidation product in the *trans*-series (**11**). Oxidation of **14** and **15** with pyridinium chlorochromate gave the corresponding aldehydes **16** and **17** (signals for aldehydic protons at δ 9.5 for each compound).

EXPERIMENTAL

General methods. — Melting points were measured on a Kofler hot-stage and are uncorrected. T.l.c. was performed on silica gel GF_{254} (Merck) with detection by charring with sulfuric acid. Column chromatography was performed on Merck silica gel (70–230 mesh). ^{1}H-N.m.r. spectra were recorded with a Varian 390 (90 MHz) or Bruker WP-360 (360 MHz) spectrometer, and ^{13}C spectra with a Bruker WP-80 (20 MHz) or WP-360 (90.5 MHz) spectrometer. Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

X-Ray data. — Crystals of 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-α-L-*erythro*-D-*galacto*-octopyranose (**15**), $C_{14}H_{22}O_7$, are orthorhombic, $P2_12_12_1$, with four molecules in the cell: a = 26.795(3), b = 9.823(1), and c = 5.8544(3) Å, and V = 1540.8(3) Å^3. A cubic crystal of edge 0.5 mm was selected and 1545 independent reflexions were measured for θ <60°, using graphite-monochromated CuKα radiation. An intensity decay of 4% was observed during the data collection. The structure was solved by MULTAN[10] with the greatest 200 e's. After anisotropic full-matrix least-squares refinement of the non-hydrogen atoms, a difference map showed the position of the hydrogen atoms[11]. These were included as fixed for a last refinement where a weighting scheme to normalise $\langle \omega \Delta F \rangle$ *vs.* $\langle F_q \rangle$ and $\langle \sin \theta/\lambda \rangle$ was used. The final R factors were R = 0.052 and R_ω = 0.58 for the 1290 observed reflexions [$I > 2\sigma(I)$]. The absolute configuration was confirmed by using 125 selected Friedel pairs with $F_c > 0.035$, for which the averaged Bijvoet difference was 0.126 for the correct enantiomer *versus* 0.177 for the wrong one. The final atomic coordinates and equivalent isotropic thermal parameters are recorded in Table I*.

*The Tables of anisotropic thermal parameters, hydrogen atom parameters, F_o–F_c data, and geometry data for the non-hydrogen atoms (including bond distances, angles, and torsion angles) are deposited with, and may be obtained from, Elsevier Science Publishers B.V., B.B.A. Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/314/*Carbohydr. Res.*, 141 (1985) 49–56.

TABLE I

CO-ORDINATES AND THERMAL PARAMETERS[a] OF $C_{14}H_{22}O_7$ (**15**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
O-1	0.5173(1)	0.2115(2)	0.2742(5)	474(7)
O-2	0.5305(1)	0.0682(2)	0.5707(5)	480(7)
O-3	0.6248(1)	−0.1214(2)	0.2714(5)	523(8)
O-4	0.6854(1)	0.0255(3)	0.3648(9)	808(14)
O-5	0.6009(1)	0.1873(2)	0.1755(4)	394(6)
O-6	0.6568(1)	0.4443(2)	0.3286(4)	450(7)
O-8	0.6878(1)	0.5123(4)	0.8714(5)	743(11)
C-1	0.5545(1)	0.1197(4)	0.1967(6)	410(9)
C-2	0.5540(1)	0.0061(3)	0.3789(7)	419(9)
C-3	0.6050(1)	−0.0425(3)	0.4544(7)	431(9)
C-4	0.6429(1)	0.0716(3)	0.4868(7)	474(10)
C-5	0.6254(1)	0.2080(3)	0.3910(5)	354(8)
C-6	0.6686(1)	0.3009(3)	0.3457(6)	397(9)
C-7	0.6873(1)	0.3962(4)	0.5159(6)	427(9)
C-8	0.6660(2)	0.4044(5)	0.7524(7)	628(13)
C-9	0.4947(1)	0.1600(4)	0.4806(7)	507(11)
C-10	0.4465(1)	0.0875(5)	0.4216(14)	880(20)
C-11	0.4878(2)	0.2745(5)	0.6469(10)	815(17)
C-12	0.6772(2)	−0.1070(4)	0.2742(7)	458(10)
C-13	0.6954(2)	−0.1179(8)	0.0322(10)	899(20)
C-14	0.7020(2)	−0.2125(5)	0.4219(9)	735(15)

[a] $U_{eq} = 1/3 \times \text{sum}[U_{ij}\, a_i^* a_j^* a_i^* a_j \cos(a_i a_j)] \times 10^{**4}$.

Wittig condensation[7]. — A solution of LiOMe (6 mmol) in MeOH (20 mL) was added during 2.5 h to a stirred mixture of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose[12] (**4**; 1040 mg, 4 mmol) and (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (2500 mg, 5.5 mmol) in anhydrous *N,N*-dimethylformamide (20 mL) under N_2 at 85°. The reaction was continued until no **4** remained (t.l.c.). The mixture was then cooled, poured into water (300 mL), and extracted with ether (5 × 100 mL). The combined extracts were dried and concentrated to yield a residue which was subjected to column chromatography (hexane–ethyl acetate, 8:2) to give a mixture (550 mg, 46%) of **5** and **6** in the ratio 3:7. These compounds were isolated but not further characterised.

Silica gel (1.5 g) impregnated with aqueous 10% oxalic acid[13] was added to a solution of **6** (600 mg) in CH_2Cl_2 (20 mL). Monitoring by t.l.c. indicated the reaction to be complete after 20 min. The silica gel was collected and washed with CH_2Cl_2, and the combined filtrate and washings were concentrated under vacuum. Column chromatography of the residue (hexane–ethyl acetate, 8:2) yielded *cis*-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enodialdo-1,5-pyranose (**12**; 420 mg, 80%) as an oil, $[\alpha]_D$ −11° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 10.1 (d, 1 H, *J* 6.0 Hz, H-8), 6.55 (dd, 1 H, *J* 12.0 and 6.0 Hz, H-6), 6.10 (ddd, 1 H, *J* 12.0, 6.0, and 1.1 Hz, H-7), 5.5 (d, 1 H, *J* 5.0 Hz, H-1); ^{13}C, 191.8 (C-8), 145.2 (C-6), 130.4 (C-7), 96.4 (C-1), 73.0 (C-4), 70.9* (C-2), 70.3* (C-3), 65.8 p.p.m. (C-5) (* assignments may be interchanged).

Aqueous 10% HCl (2.5 mL) was added to a solution of the mixture of **5** and **6** (100 mg) in tetrahydrofuran at room temperature. The hydrolysis was complete after 2 h (t.l.c.). The solution was neutralised with $NaHCO_3$ and extracted with $CHCl_3$ to give *trans*-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enodialdo-1,5-pyranose (**7**; 77 mg, 90%), m.p. 80–84° (from hexane–acetone), $[\alpha]_D$ −140° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 9.6 (d, 1 H, *J* 7.5 Hz, H-8), 6.8 (dd, 1 H, *J* 3.5 and 15.3 Hz, H-6), 6.35 (ddd, 1 H, *J* 1.4, 15.3, and 7.5 Hz, H-7), 5.6 (d, 1 H, *J* 5.0 Hz, H-1); ^{13}C, 193.8 (C-8), 151.5 (C-6), 132.8 (C-7), 96.5 (C-1), 72.7 (C-4), 71.0* (C-3), 70.5* (C-2), 67.7 p.p.m. (C-5).

Anal. Calc. for $C_{14}H_{22}O_6$: C, 58.7; H, 7.75. Found: C, 58.6; H, 7.3.

Reduction of **7**. — Compound **7** (100 mg) was treated with $NaBH_4$ (100 mg) in MeOH (10 mL) at 0°. The reduction was complete after 30 min. Excess of $NaBH_4$ was destroyed by the addition of acetone, and the solution was poured into H_2O and extracted with $CHCl_3$ to give *trans*-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose (**8**, 80 mg) as an oil, $[\alpha]_D^{25}$ −10° (*c* 0.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.7 (m, 2 H, H-8,8); ^{13}C, 132.8 (C-6), 126.9 (C-7), 96.5 (C-1), 73.5 (C-4), 70.9* (C-2), 70.5* (C-3), 68.3 (C-5), 62.9 p.p.m. (C-8).

trans-*6,7,8-Trideoxy-1,2:3,4-di-*O*-isopropylidene-α-*D-galacto-*oct-6-enopyranose* (**9**). — To a solution of **8** (100 mg) in anhydrous tetrahydrofuran (4 mL) containing Et_3N (0.2 mL) at −20° was added MsCl (0.1 mL). After 3 h, $LiAlH_4$ (50 mg) was added and the temperature of the mixture was allowed to rise slowly to room temperature. Excess of $LiAlH_4$ was destroyed by the addition of H_2O and aqueous NaOH, and the aqueous solution was extracted with $CHCl_3$ to give **9** (65 mg, 66%), m.p. 235–237° (from hexane–ethyl acetate), $[\alpha]_D^{25}$ −99° (*c* 0.75, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.65 (m, 2 H, H-6,7), 5.50 (d, 1 H, *J* 5.0 Hz, H-1), 1.7 (d, 3 H, *J* 5.0 Hz, H-8); ^{13}C, 130.0 (C-6), 126.9 (C-7), 96.6 (C-1), 73.8 (C-4), 71.0* (C-3), 70.6* (C-2), 69.1 (C-5), 17.9 p.p.m. (C-8).

Anal. Calc. for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 60.79; H, 8.45.

Epoxidation of **9**. — To a solution of **9** (65 mg) in CH_2Cl_2 (10 mL) was added *m*-chloroperbenzoic acid (80 mg). The mixture was stirred at room temperature for 2 h, then diluted with CH_2Cl_2, and washed with aqueous Na_2SO_3 and $NaHCO_3$. The CH_2Cl_2 layer was dried and concentrated, and the residue was subjected to column chromatography (hexane–ethyl acetate, 8:2) to give 6,7-anhydro-8-deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octopyranose (**10**, 10 mg) as an oil, $[\alpha]_D^{20}$ −63° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.65 (d, 1 H, *J* 4.5 Hz, H-1), 3.0 (m, 2 H, epoxide protons), 1.4 (d, 3 H, *J* 4.5 Hz, H-8); ^{13}C, 96.3 (C-1), 72.0 (C-4), 70.7* (C-3), 70.4* (C-2), 69.6 (C-5), 58.0 (C-6), 51.3 (C-7), 17.4 p.p.m. (C-8).

Eluted second was 6,7-anhydro-8-deoxy-1,2:3,4-di-*O*-isopropylidene-α-L-*erythro*-D-*galacto*-octopyranose (**11**, 40 mg) as an oil, $[\alpha]_D^{20}$ −78° (*c* 2, chloroform). N.m.r. data: ^1H, δ 5.55 (d, 1 H, *J* 4.5 Hz, H-1), 2.95 (m, 2 H, epoxide protons), 1.4 (d, 3 H, overlapped with signals for CMe_2, H-8); ^{13}C, 96.1 (C-1), 71.2 (C-4), 70.5* (C-3), 70.4* (C-2), 68.7 (C-5), 56.7 (C-6), 54.7 (C-7), 17.3 p.p.m. (C-8).

*6,7-Anhydro-1,2:3,4-di-*O*-isopropylidene-α-*D-erythro-D-galacto-*octopyranose* (**14**) *and the* L-erythro-D-galacto *isomer* (**15**). — The reduction of **12** was carried out as described above for **7**, to give *cis*-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranose (**13**), isolated as an oil, $[\alpha]_D^{25}$ −10° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): ^{13}C, 133.3 (C-6), 127.5 (C-7), 96.6 (C-1), 73.3 (C-4), 70.9* (C-3), 70.4* (C-2), 64.3 (C-5), 59.2 p.p.m. (C-8).

m-Chloroperbenzoic acid (150 mg) was added to a solution of **13** (180 mg) in CH_2Cl_2 (15 mL). The solution was stirred at room temperature for 5–6 h, then diluted with CH_2Cl_2, washed with aqueous 10% Na_2SO_3 and saturated aqueous $NaHCO_3$, dried, and concentrated. Column chromatography (hexane–ethyl acetate, 85:15) of the residue yielded **14** (35 mg), m.p. 85–87° (from hexane–ether), $[\alpha]_D^{20}$ −92° (*c* 0.15, chloroform). N.m.r. data ($CDCl_3$, 360 MHz): ^1H, δ 5.5 (d, 1 H, *J* 5.0 Hz, H-1), 4.6 (dd, 1 H, *J* 2.5 and 7.5 Hz, H-3), 4.4 (dd, 1 H, *J* 7.5 and 1.5 Hz, H-4), 4.3 (dd, 1 H, *J* 5.0 and 2.5 Hz, H-2), 3.9 (dd, 1 H, *J* 11.0 and 5.0 Hz, H-8), 3.7 (dd, 1 H, *J* 5.0 and 11.0 Hz, H-8), 3.63 (dd, 1 H, *J* 7.0 and 1.5 Hz, H-5), 3.40 (dd, 1 H, *J* 7.0 and 11.0 Hz, H-6), 3.3 (m, 1 H, H-7); ^{13}C, 96.3 (C-1), 71.4 (C-4), 70.6* (C-3), 70.6* (C-2), 66.3 (C-5), 60.8 (C-8), 55.6 (C-6), 53.4 p.p.m. (C-7).

Anal. Calc. for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34. Found: C, 55.42; H, 7.40.

Eluted second was **15** (100 mg), m.p. 122–124° (from hexane–acetone), $[\alpha]_D^{25}$ −83° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$, 360 MHz): ^1H, δ 5.60 (d, 1 H, *J* 5.0 Hz, H-1), 4.60 (dd, 1 H, *J* 7.5 and 2.5 Hz, H-3), 4.30 (dd, 1 H, *J* 5.0 and 2.5 Hz, H-2), 4.2 (dd, 1 H, *J* 7.5 and 2.0 Hz, H-4), 3.90 (dd, 1 H, *J* 12.0 and 4.0 Hz, H-8), 3.80 (m, 2 H, H-5,8), 3.30 (m, 2 H, H-6,7); ^{13}C, 96.3 (C-1), 71.2 (C-4), 70.8* (C-2), 70.3* (C-3), 67.3 (C-5), 60.4 (C-8), 56.1* (C-6), 55.7* p.p.m. (C-7).

Anal. Calc. for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34. Found: C, 55.90; H, 7.41.

Oxidation of **14** *and* **15**. — To a solution of **15** (80 mg) in CH_2Cl_2 (10 mL) was added pyridinium chlorochromate (350 mg), and the mixture was stirred for 2 h, then diluted with CH_2Cl_2, and filtered through a short column of silica gel. The column was washed with ether (50 mL) to give 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-α-L-*erythro*-D-*galacto*-octodialdo-1,5-pyranose (**17**, 65 mg) as an oil, $[\alpha]_D^{20}$ −32° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 9.50 (d, 1 H, *J* 5.0 Hz, H-8), 5.55 (d, 1 H, *J* 5.0 Hz, H-1), 4.60 (dd, 1 H, *J* 7.5 and 2.5 Hz, H-3), 4.30 (dd, 1 H, *J* 5.0 and 2.5 Hz, H-2), 4.05 (dd, 1 H, *J* 7.5 and 2.0 Hz, H-4), 3.85 (m, 1 H, H-5), 3.55 (m, 2 H, H-6,7); ^{13}C, 197.4 (C-8), 96.1 (C-1), 71.7 (C-4), 70.6* (C-3), 70.1* (C-2), 66.3 (C-5), 58.0 (C-7), 56.8 p.p.m. (C-6).

Oxidation of **14**, as described for **15**, gave 6,7-anhydro-1,2:3,4-di-*O*-isopropylidene-α-D-*erythro*-D-*galacto*-octodialdo-1,5-pyranose (**16**) as a thick oil, $[\alpha]_D^{20}$ −68° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 9.5 (d, 1 H, *J* 4.5 Hz, H-8), 5.5 (d, 1 H, *J* 5.0 Hz, H-1), 3.55 (m, 2 H, H-6,7); ^{13}C, 197.4 (C-8), 96.1 (C-1), 71.2 (C-4), 70.5* (C-3), 70.2* (C-2), 65.1 (C-5), 57.6* (C-7), 57.5* p.p.m. (C-6).

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