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A Highly Diastereoselective Synthesis of 4-Octulose and 2-Deoxy-4-octulose from a D-Fructose derivative[1]

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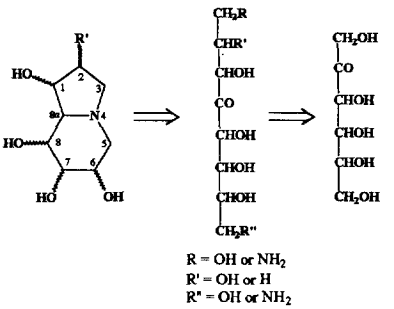
Abstract: Bishydroxylation of methyl (*Z*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranosonate **1** with osmium tetraoxide proceeded with extremed high diastereoselectivity to give only methyl 4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate **2**. Configurations of the new stereogenic centers (C-2,3) in **2** were determined by degradation of the C-5,6,7,8 fragment to the well-known methyl 2,3,4-tri-*O*-methyl-D-(+)-erythronate **7**. Transformation of **2** into the required D-*arabino*-L-*erythro*-oct-4-ulosa **10**, was achieved by a methodology that implied, protection to **8**, reduction of the ester group in **8** to a hydroxymethyl group in **9**, and finally deprotection to the free D-*arabino*-L-*erythro*-oct-4-ulosa **10**. On the other hand, epoxidation reaction on (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranose **11** afforded only the corresponding 2,3-*anhydro* derivative **12** with β-D-*arabino*-D-*threo* configuration, as could be demonstrated by degradation to (*S*)-1,2,4-trimetoxybutane **16**, which synthesis is reported herein.

Potent glycosidase inhibitors, such as polyhydroxyindolizidines[2], have received much attention in recent years because of their potential as antitumor, anti-HIV, antidiabetic agents, etc. Retrosynthesis of such molecules (see Scheme I), clearly demonstrates that 4-octuloses could be excellent chiral intermediates, since only the introduction, either at C-1 or C-8, of an amino group would be necessary that would form, by internal reductive-amination process of the ketone at C-4, the required pyrrolidine or piperidine ring, and finally a new cyclization to the indolizidine ring, by internal nucleophilic displacement, of the appropriate derivative. On the other hand, the cheaper and readily available D-fructose and L-sorbose, can be considered excellent starting chiral templates for the enantioselective synthesis of such 4-octuloses, and therefore of the above inhibitors, the choice depending on the required stereoisomers. An extension of the sugar chain would be necessary by two more carbon atoms at C-1, insertion in a regio and stereocontroled manner of one or two hydroxyl groups on such an extended chain to afford either a 4-octulose or a 2-deoxy-4-octulose.

Although the configurations of the stereogenic centres at C-6,7,8 are predetermined by the starting hexulose, those of the new ones created (C-1,2, see Scheme I) will depend on the stereochemistry of the intermediate unsaturated compound as well as that of the bishydroxylation process used. Thus, in a previous paper[1] we described the synthesis of 4-octuloses with the D-*arabino*-L-*threo* and D-*arabino*-D-*threo* configurations by catalytic osmylation of methyl (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranosonate followed by the appropriate transformations. We report herein the results obtained when the (*Z*)-isomer[1] **1** of the latter compound

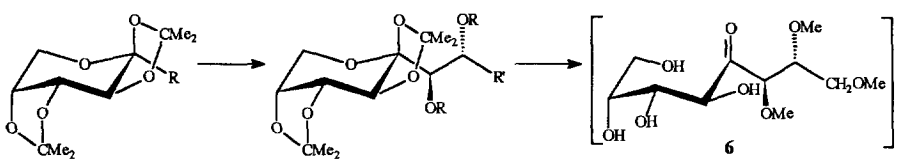
[1] Synthesis of 4-Octuloses, Part II. For Part I, see Ref. 1.

Scheme I



and (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranose[3] **11** are subjected to bishydroxylation and epoxidation, respectively.

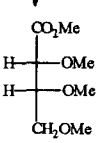
Bishydroxylation of methyl (*Z*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranosonate **1** with osmium tetraoxide[4] gave exclusively methyl 4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate **2**.



1 R = (*Z*)-CH=CHCO$_2$Me
11 R = (*E*)-CH=CHCH$_2$OH

2 R = H; R' = CO$_2$Me
3 R = Me; R' = CO$_2$Me
4 R = Me; R' = CH$_2$OH
5 R = Me; R' = CH$_2$OMe
8 R = CMe$_2$: R' = CO$_2$Me
9 R = CMe$_2$: R' = CH$_2$OH

6



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Although in some instances, the configuration of the osmylation product of an unsaturated compound with an adjacent stereogenic centre bearing either a hydroxyl or alkoxyl group, can be predicted by application of Kishi's empirical rule,[5] which states "that the relative stereochemistry between the preexisting hydroxyl or alkoxyl group at the adjacent stereogenic center and the new-introduced hydroxy group, of the major product, is *erythro*", which involves a preferential *anti* approach of OsO_4 to such adjacent groups. In our case, the presence of two α-alkoxy groups at C-4 in **1** would introduce some uncertainty about which of the two faces of the carbon-carbon double bond, in the less compressed conformation of **1**[6-8] (see Fig. 1), would be attacked according to such a rule.

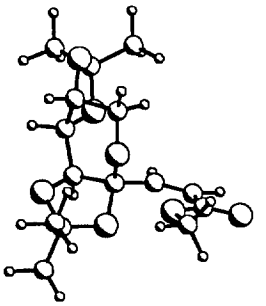
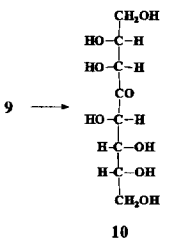


Fig. 1. Less compressed conformation for **1**

Thus, it was necessary to make a stereochemical correlation between the two new-formed hydroxyl groups with a compound of known absolute configuration, in our case, methyl 2,3,4-tri-*O*-methyl-(+)-D-erythronate[9] **7**. In this way, compound **2** was transformed into the corresponding 2,3-di-*O*-methyl derivative **3** which was reduced with $LiAlH_4$ to 4,5:6,7-di-*O*-isopropylidene-2,3-di-*O*-methyl-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranose **4**. Compound **4** was methylated to the related 1,2,3-tri-*O*-methyl derivative **5** which was hydrolyzed to the not characterized 1,2,3-tri-*O*-methyl-D-*arabino*-L-*erythro*-oct-4-ulose **6** and subsequently oxidized with $NaIO_4$ to the not isolated 2,3,4-tri-*O*-methyl-(+)-D-erythronic acid, that, after treatment with diazomethane gave the above mentioned methyl ester **7**, showing 2*S*,3*R* configurations for the two new-formed stereogenic centers in **4**. From these results it could be concluded that in the present case, the stereoselectivity of the bishydroxylation seems to be controlled by steric (the β-face in Fig.1 is more accessible) rather than by stereoelectronic effects.

Compound **2** was acetonated with acetone/PTSA/$CuSO_4$ affording methyl 2,3:4,5:6,7-tri-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate **8**. On the other hand, compound **8** was reduced with $LiAlH_4$ to the corresponding octulose derivative **9**. Finally, compound **9** upon treatment with aqueous trifluoroacetic acid gave the expected D-*arabino*-L-*erythro*-oct-4-ulose **10**.



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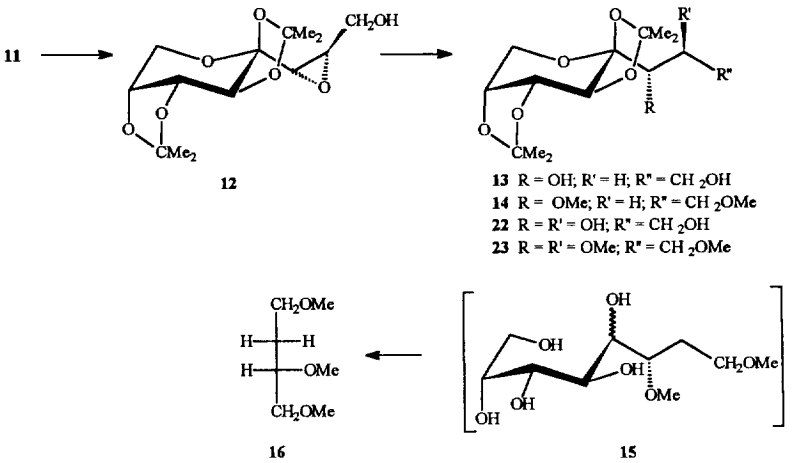
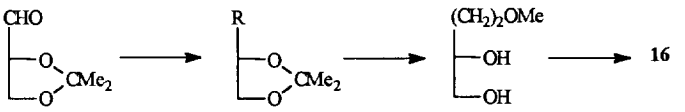
As has been previously stated, 2-deoxy-4-octulose derivatives (see Scheme I) are also important key intermediates in the synthesis of the indolizidine type glycosidase inhibitors and in order to see the stereochemical course of such synthetic processes, the epoxidation reaction of (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-

4-ulo-4,8-pyranose[3] **11** with *m*-chloroperbenzoic acid, was carried out. From this reaction, only 2,3-*anhydro*-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-D-*threo*-oct-4-ulo-4,8-pyranose **12** could be isolated and characterized as follows:



Action of bis(2-methoxyethoxy)aluminium hydride (Red-Al) on **12**, caused a highly regioselective opening[10] of the 2,3-oxirane ring to afford the 1,3-diol, namely 2-deoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*gluco*-oct-4-ulo-4,8-pyranose **13**. Compound **13** was methylated to the corresponding 1,3-di-*O*-methyl derivative **14**, that upon hydrolysis and reduction to the not characterized 1,3-di-*O*-methyl-2-deoxyoctitol **15** followed by degradation of its polyhydroxylalkylic chain, reduction and methylation, (*S*)-1,2,4-trimethoxybutane **16**. Compound **16**, that was selected by us as a stereochemical correlation patron, was synthesized from 2,3-*O*-isopropylidene-D-glyceraldehyde[11] **17** as indicated below:



17

18 R = CH=CH2
19 R = (CH2)2OH
20 R = (CH2)2OMe

21

Reaction of **17** with methylenetriphenylphosphorane gave (*S*)-1,2-*O*-isopropylidene-but-3-ene-1,2-diol **18** that was regioselectively hydrated ($Me_2S{:}BH_3/H_2O_2$,OH^-) to (*S*)-1,2-*O*-isopropylidene-1,2,4-butanetriol **19** that after methylation to **20**, deacetonation to **21** and finally di-*O*-methylation gave **16**, which showed the same mass spectrum fragmentation pattern to that recorded for the (*RS*)-form[12]. In addition, the stereochemistry of **12** was also confirmed by transformation into 4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-D-*erythro*-oct-4-ulo-4,8-pyranose **22**, through a Payne-rearrangement[13] product, that after methylation gave the corresponding tri-*O*-methyl derivative **23**, namely

4,5:6,7-di-*O*-isopropylidene-1,2,3-tri-*O*-methyl-β-D-*arabino*-D-*erythro*-oct-4-ulo-4,8-pyranose **23** which showed different optical and spectroscopic properties to those of **5**, and hence different configurations at C-2,3.

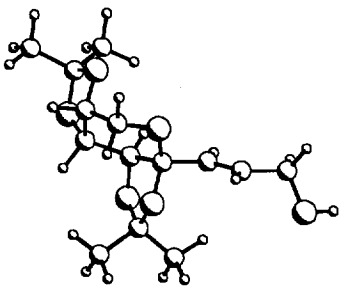


Fig. 2. Less compressed conformation for **11**

The high stereoselectivity found in the epoxidation reaction would result from a preferential attack of the peracid, by the more accessible β-face, one of the methyl substituent partially block the α-face, in the less compressed conformation of **11**[6-8] (see Fig. 2).

Experimental

General: Melting points were determined with a Gallenkamp apparatus and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under reduced pressure. The ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-300 and ARX-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). IR spectra were recorded with a Perkin-Elmer 782 instrument and mass spectra with a Fisons mod. Platform II and VG Autospec-Q mass spectrometers. Optical rotations were measured for solutions in $CHCl_3$ (1-dm tube) with a Jasco DIP-370 polarimeter. GLC was performed on a Perkin-Elmer 8410 gas chromatograph equipped with a flame-ionisation detector and a steel column (2 m x 0.125 in. i.d.) packed with 5% OV-17 on Chromosorb W (100-120 mesh): (*A*) at 150°C, (*B*) at 200°C. The He flow rate was 30 mL/min, the injection port and the zone-detector temperatures were 250°C. TLC was performed on precoated silica gel 60 F_{254} aluminium sheets and detection by charring with H_2SO_4. Column chromatography was performed on silica gel (Merck, 7734). Some of the noncrystalline compounds, for which elemental analyses were not obtained were shown to be homogeneous by chromatography and characterised by NMR and mass spectrometry.

Bishydroxylation of 1: To a stirred solution of **1** (1.85 g, 5.9 mmol) in acetone (20 mL), 4-methylmorpholine *N*-oxide (690 mg, 5.9 mmol) and aqueous 1% osmium tetraoxide (4 mL) were added, and the mixture left at room temperature dor 4 days. TLC (ether) then revealed the presence of a new slower-running product. The mixture was concentrated to a residue that was extracted with ethyl acetate, then concentrated. Column chromatography (2:1 ether-hexane) afforded crystalline methyl 4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate (**2**, 1.64 g, 80%), m.p.: 123-125°C (from ether), $[\alpha]_D^{21}$: +2, $[\alpha]_{405}^{21}$: +19 (c 1.1); ν_{max}^{KBr} 3455 and 3387

(OH), and 1749 cm^{-1} (CO). NMR data: ^1H, δ 4.58 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,7}$ 8.0 Hz, H-6), 4.47 (d, 1 H, H-5), 4.36 (bs, 1 H, H-2), 4.17 (bdd, 1 H, H-7), 4.06 (bs, 1 H, H-3), 3.82 (dd, 1 H, $J_{7,8a}$ 1.8, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.71 (s, 3 H, OMe), 3.65 (bd, 1 H, H-8*e*), 1.49, 1.46, 1.39, and 1.30 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 172.26 (C-1), 109.42 and 109.12 (2 CMe_2), 103.83 (C-4), 72.63, 72.24, 70.69, 70.55 and 70.05 (C-2,3,5,6,7), 61.70 (C-8), 52.18 (OMe), 26.70, 25.58, 25.47 and 23.83 (2 CMe_2). Anal. Calcd. for $C_{15}H_{24}O_9$: C, 51.72; H, 6.94. Found: C, 51.28; H, 6.86.

Methyl 4,5:6,7-di-*O*-isopropylidene-2,3-di-*O*-methyl-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate 3: To a stirred solution of NaH (80% oil dispersion) (270 mg, 9 mmol)) in dry Me_2SO (7 mL) and imidazole (175 mg) under Ar, a solution of **2** (1 g, 2.9 mmol) in dry THF (10 mL) was added dropwise at room temperature. The mixture was maintained at 60° for 30 min. Then yodomethane (0.5 mL, 9 mmol) was added and the mixture stirred for additional 30 min. TLC (ether) then showed a faster-running product, the excess of hydride was destroyed by cautious addition of ether saturated with water and water. The organic phase was separated and the aqueous extracted with ether. The extracts were washed with brine and concentrated. Column chromatography (1:3 → 1:1 ether-hexane) of the residue afforded syrupy **3** (0.7 g, 65%), $[\alpha]_D^{26}$: -18 $[\alpha]_{405}^{26}$: -35 (c 1.4); ν_{max}^{film}1752 (C=O), 1383 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.57 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,7}$ 8 Hz, H-6), 4.36 (d, 1 H, H-5), 4.28 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 4.18 (bdd, 1 H, H-7), 3.83 (dd, 1 H, $J_{7,8a}$ 1.9, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.71 (s, 3 H, CO_2Me), 3.70 (dd, 1 H, $J_{7,8e}$ 0.5 Hz, H-8*e*), 3.58 (d, 1 H, H-3), 3.50 and 3.39 (2 s, 6 H, 2 OMe), 1.49, 1.48, 1.34, and 1.31 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 170.75 (C-1), 108.97 and 108.86 (2 CMe_2), 103.30 (C-4), 84.17 (C-3), 80.50 (C-2), 70.77 (C-7), 70.36 (C-5,6), 61.35 (C-8), 60.46 and 58.53 (2 OMe), 51.70 (CO_2Me), 26.68, 25.86, 25.48, and 24.03 (2 CMe_2). Mass spectrum (c.i., CH_4): *m/z* 379 (2.8%, M^++3), 378 (14.5, M^++2), 377 (100, M^++1), 361 (16.3, M^+-Me), 319 (13.1, M^++1-Me_2CO), 287 (80.8, M^++1-Me_2CO-MeOH) and 59 (19.9, Me_2COH^+). Anal. Calcd. for $C_{17}H_{28}O_9$: C, 54.24; H, 7.50. Found: C, 54.38; H, 7.26.

4,5:6,7-Di-*O*-isopropylidene-2,3-di-*O*-methyl-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranose 4: To a stirred solution of **3** (650 mg, 1.73 mmol) in dry ether (7 mL) $LiAlH_4$ (70 mg, 1.83 mmol) was added portionwise and the mixture left at room temperature for 30 min. TLC (ether) then showed the presence of a slower-running product. The excess of hydride was destroyed by cautious addition of aqueous saturated amonium chloride solution, filtered, concentrated and the residue extracted with ether. Concentration of the extracts gave a residue that was chromatographed (2:1 ether-hexane) to afford **4** (544 mg, 90.3%) as a colourless syrup, $[\alpha]_D^{26}$: -12, $[\alpha]_{405}^{26}$: -24 (c 1.2); ν_{max}^{film}3521 (OH), 1383 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.61 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,7}$ 7.9 Hz, H-6), 4.38 (d, 1 H, H-5), 4.21 (bdd, 1 H, H-7), 3.89 (dd, 1 H, $J_{1,2}$ 4.6, $J_{1,1'}$ 11.3 Hz, H-1), 3.84 (dd, 1 H, $J_{7,8a}$ 1.8, $J_{8a,8e}$ 12.9 Hz, H-8a), 3.81 (d, 1 H, $J_{2,3}$ 5.2 Hz, H-3), 3.76-3.72 (m, 1 H, H-2) (d, 1 H, H-8'), 3.70 (bd, 1 H, H-8*e*), 3.58 (dd, 1 H, $J_{1',2}$ 2.24 Hz, H-1'), 3.54 and 3.40 (2 s, 6 H, 2 OMe), 2.35 (bs, 1 H, HO-1), 1.48, 137, and 1.34 (3 s, 12 H, 2 CMe_2); ^{13}C, δ 109.03 (2 CMe_2), 103.17 (C-4), 81.98 (C-3), 81.52 (C-2), 70.97 (C-7), 70.38 and 70.34 (C-5,6), 61.61 and 61.24 (C-1,8), 26.58, 26.10, 25.42, and 24.19 (2 CMe_2). Mass spectrum (c.i., CH_4): *m/z* 349 (4.5%, M^++1), 348 (11.8,

M^+), 331 (100, M^++1-H_2O), 291 (43.9, M^++1-Me_2CO), 273 (78.0, M^++1-H_2O-Me_2CO), 241 (52.6, M^++1-H_2O-Me_2CO-MeOH), 147 (51.0), and 59 (32.9, Me_2COH^+).

4,5:6,7-Di-*O*-isopropylidene-1,2,3-tri-*O*-methyl-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranose 5: To a stirred solution of NaH (80% oil dispersion) (90 mg, 3 mmol)) in dry Me_2SO (5 mL) and imidazole (50 mg) under Ar, a solution of **4** (505 mg, 1.45 mmol) in dry THF (5 mL) was added dropwise at room temperature. The mixture was maintained at 60° for 30 min. Then yodomethane (0.5 mL, 9 mmol) was added and the mixture stirred for additional 30 min. TLC (ether) then showed a faster-running product, the excess of hydride was destroyed by cautious addition of ether saturated with water and water. The organic phase was separated and the aqueous extracted with ether. The extracts were washed with brine and concentrated. Column chromatography (1:3 ether-hexane) of the residue afforded syrupy **5** (380 mg, 72.4%), $[\alpha]_D^{25}$: -4, $[\alpha]_{405}^{25}$: -5.5 (c 1.4); ν_{max}^{film}1383 and 1373 (CMe_2), and 1114 cm^{-1} (C-O-C). NMR data: ^1H, δ 4.60 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,7}$ 7.9 Hz, H-6), 4.39 (d, 1 H, H-5), 4.20 (bdd, 1 H, H-7), 3.91-3.88 (m, 1 H, H-2), 3.84 (dd, 1 H, $J_{7,8a}$ 1.8, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.80 (dd, 1 H, $J_{1,2}$ 2, $J_{1,1'}$ 11.3 Hz, H-1), 3.70 (d, 1 H, H-8*e*), 3.58 (d, 1 H, H-3), 3.54-3.48 (m, 2 H, H-3,1'), 3.51, 3.41 and 3.36 (3 s, 9 H, 3 OMe), 1.48, 1.35, and 1.34 (3 s, 12 H, 2 CMe_2); ^{13}C, δ 108.95 and 108.82 (2 CMe_2), 103.19 (C-4), 81.35 and 81.31 (C-2,3), 73.55 (C-1), 71.07, 70.49, and 70.25 (C-5,6,7), 61.24 (C-8), 60.96, 59.13 and 57.60 (3 OMe), 26.61, 26.13, 25.56, and 24.23 (2 CMe_2). Mass spectrum (c.i., CH_4): *m/z* 365 (2.3%, M^++3), 364 (13.6, M^++2), 363 (100, M^++1), 347 (14.5, M^+-Me), 331 (5.4, M^++1-MeOH), 305 (15.2, M^++1-Me_2CO), 274 (14.7, M^++2-Me_2CO-MeOH), 273 (78.2, M^++1-Me_2CO-MeOH), 241 (32.8, (M^++1-Me_2CO-2MeOH), 229 (33.6), 101 (31.9, $C_5H_9O_2^+$) and 59 (24.2, Me_2COH^+). Anal. Calcd. for $C_{17}H_{30}O_8$: C, 56.34; H, 8.34. Found: C, 56.48; H, 8.18.

Degradation of 5 to 7: A solution of **5** (350 mg, 1 mmol) in aqueous 75% trifluoroacetic acid (4 mL) was left at room temperature for 2 days. TLC (ether) then revealed a non mobile compound. The mixture was concentrated and repeatly codistilled with water and the residue chromatographed (chloroform → 10:1 chloroform-methanol) to afford a colourless solid foam (200 mg, 71%), presumably 1,2,3-tri-*O*-methyl-D-*arabino*-L-*erythro*-oct-4-ulose (**6**) that was not further characterized but oxidised in water (5 mL) with a solution of $NaIO_4$ (0.76 g, 3.6 mmol) in the same solvent (10 mL). The reaction was monitorized by polarimetry to a constant rotation [$[\alpha]_D^{26}$ -4 → +17 (c 4, water)] after 24 h at room temperature. The mixture was concentrated and the residue extracted with ethyl acetate. Concentration of the extracts gave a residue that was dissolved in dry methanol (10 mL) and saturated with a stream of CH_2N_2 until a slight yellow colour remained and the mixture left at room temperature for 30 min. GLC (*A*) then revealed a main product with a T_R 2.24 min. The reaction mixture was concentrated and the residue chromatographed (ether) to afford methyl 2,3,4-tri-*O*-methyl-(+)-D-erythronate (**7**, 50 mg) which had $[\alpha]_D^{27}$: +22.6 (c 1.1, water), [Lit.[9] $[\alpha]_D^{21}$: +19 (c 1.04, water)]; ν_{max}^{film}1753 (C=O), 1196 and 1118 cm^{-1} (C-O-C). NMR data, ^1H δ 3.94 (d, 1 H, $J_{2,3}$ 4.5 Hz, H-2), 3.75 (s, 3 H, CO_2Me), 3.62 (dt, 1 H, H-3), 3.54 (dd, 1H, $J_{3,4}$ 4.6, $J_{4,4'}$ 10.3 Hz, H-4), 3.48 (dd, 1 H, $J_{3,4'}$ 5.7 Hz, H-4'), 3.42, 2.41, and 3.33 (3 s, 9 H, 3 OMe); ^{13}C δ 171.11 (C-1), 80.87 (C-2), 80.21 (C-3), 70.81 (C-4), 59.27, 58.98, and 58.55 (3 OMe), and 52.02 (CO_2OMe).

Methyl 2,3:4,5:6,7-tri-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranosonate 8: To a stirred solution of **2** (1.35 g, 3.9 mmol)] in dry acetone (20 mL), 2,2-dimethoxypropane (2 mL), PTSA (100 mg) and anhydrous copper sulfate (1.5 g) were added at room temperature. The stirring was continued for 4 days. TLC (ether) then revealed a faster-running product. The mixture was neutralized (K_2CO_3), filtered through a Cellite pad, and then concentrated to a residue that was chromatographed (1:3 ether-hexane) to afford syrupy **8** (1.21 g, 80%), $[\alpha]_D^{26}$: +15.5 (c 1,24); ν_{max}^{film}1764 (C=O), 1383 and 1372 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.62 (d, 1 H, $J_{2,3}$ 6.6 Hz, H-2), 4.57 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,7}$ 7.8 Hz, H-6), 4.50 (d, 1 H, H-5), 4.38 (d, 1 H, H-3), 4.20 (dd, 1 H, H-7), 3.81 (dd, 1 H, $J_{7,8a}$ 1.9, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.70 (d, 1 H, H-8*e*), 3.64 (s, 3 H, OMe), 1.64, 1.45, 1.44, 1.36, 1.35 and 1.32 (6 s, 18 H, 3 CMe_2); ^{13}C, δ 171.00 (C-1), 110.91, 109.27 and 109.11 (3 CMe_2), 101.82 (C-4), 79.64 (C-2), 75.11 (C-3), 71.13 (C-5), 70.95 (C-7), 70.29 (C-6), 61.24 (C-8), 51.75 (OMe), 26.50, 26.45, 26.04, 26.00, 25.11, and 24.32 (3 CMe_2). Mass spectrum: *m/z* 389 (1.4%, M^++1), 374 (3.4, M^++1-Me), 373 (28.2, M^+-Me), 331 (1.0, M^++1-Me_2CO), 330 (1.1, M^+-Me_2CO), 329 (5.9, M^++1-AcOH), 315 (5.0, M^+-Me-Me_2CO), 313 (5.3, M^+-Me-AcOH), 273 (1.4 M^++1-2Me_2CO). 272 (1.9 M^+-2Me_2CO), 271 (9.3 M^++1-AcOH-Me_2CO), 257 (4.8, M^+-Me-2Me_2CO), 256 (2.9, M^++1-Me-Me_2CO-AcOH), 255 (17.1, M^+-Me-Me_2CO-AcOH), 229 (14.7, M^++2-Me_2CO-MeOH), 229 (30.2, M^++1-$C_7H_{12}O_4$), 171 (42.8, M^++1-Me_2CO-$C_7H_{12}O_4$), 85 (57.7, $C_4H_5O_2^+$), 59 (71, Me_2COH^+), and 43 (100, Ac^+).

2,3:4,5:6,7-Tri-*O*-isopropylidene-β-D-*arabino*-L-*erythro*-oct-4-ulo-4,8-pyranose 9: A stirred solution of **8** (0.5 g, 1.3 mmol) in anhydrous ether (10 mL) was treated with $LiAlH_4$ (100 mg) at room temperature for 30 min. TLC (ether) then revealed the presence of a slower-running compound. Work-up of the reaction mixture as above afforded, after column chromatography (2:1 ether-hexane), crystalline **9** (400 mg, 86%), m.p.: 98-99°C (from ether), $[\alpha]_D^{25}$: -9.7, $[\alpha]_{405}^{25}$: -20.1 (c 1.04); ν_{max}^{film}3544 (OH), 1387 and 1374 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.60 (dd, 1 H, $J_{5,6}$ 2.7, $J_{6,7}$ 7.9 Hz, H-6), 4.47 (d, 1 H, H-5), 4.31 (dt, 1 H, $J_{1,2}$ = $J_{2,3}$ = 6.6, $J_{1',2}$ 4.2 Hz, H-2), 4.29 (d, 1 H, H-3), 4.21 (dd, 1 H, $J_{7,8a}$ 1.4 Hz, H-7), 3.91-3.85 (m, 2 H, H-1,8*a*), 3.77 (dd, 1 H, $J_{1,1'}$ 12.1, Hz, H-1'), 3.71 (d, 1 H, $J_{8a,8e}$ 13 Hz, H-8*e*), 2.10 (bs, 1 H, HO-1), 1.52, 1.47, 1.45, 1.42, 1.34, and 1.33 (6 s, 18 H, 3 CMe_2); ^{13}C, δ 109.67, 109.20, and 108.51 (3 CMe_2), 102.96 (C-4), 78.21 (C-2), 77.10 (C-3), 71.59 (C-5), 70.77 (C-7), 70.11 (C-6), 61.94 (C-1), 61.35 (C-8), 26.92, 26.70, 25.96, 25.58, 25.26, and 24.12 (3 CMe_2). Anal. Calcd. for $C_{17}H_{28}O_8$: C, 56.65; H, 7.83. Found: C, 56.76; H, 8.01.

D-*Arabino*-L-*erythro*-oct-4-ulose 10: A solution of **9** (82 mg, 0.21 mmol) in aqueous 50% trifluoroacetic acid (3 mL) was left at room temperature for 50 h. TLC (ethyl acetate) then revealed that **9** had disappeared and that a non-mobile substance was present. The mixture was concentrated and residue acetic acid was removed by codistillation with water to a residue that was chromatographed (2:1 chloroform-methanol) to afford syrupy **10** (32 mg, 64%) that was homogeneous by TLC and had $[\alpha]_D^{28}$: +15 (c 1.84, methanol).

Epoxidation of 11: To a stirred solution of (*E*)-2,3-dideoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-oct-2-ene-4-ulo-4,8-pyranose[3] (**11**, 2.74 g, 9.58 mol) in dry Cl_2CH_2 (25 mL), 60% MCPBA (3 g, 10.4 mmol) was added. After 24 h, GLC (*B*) then revealed the absence of **11** (T_R 6.38 min) and the presence of a new compound (T_R 7.73 min).

The mixture was filtered and the filtrate washed with aqueous sodium thiosulfate, saturated sodium carbonate solution and water, then concentrated. Column chromatography (1:2 ether-hexane → ether) of the residue yielded syrupy 2,3-*anhydro*-4,5:6,7-di-*O*-isopropylidene-β-D-*arabino*-D-*threo*-oct-4-ulo-4,8-pyranose (**12**, 2.41 g, 83.4%); $[\alpha]_D^{23}$: -18 (c, 0.5); ν_{max}^{film}3482 (OH), 1384 and 1374 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.52 (dd, 1 H, $J_{5,6}$ 2.4, $J_{6,7}$ 8 Hz, H-6), 4.23 (dd, 1 H, $J_{7,8a}$ 1.4 Hz, H-7), 4.01 (d, 1 H, H-5), 3.92 (dd, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 3.86 (dd, 1 H, H-8*a*), 3.74 (d, 1 H, $J_{8a,8e}$ 12.7 Hz, H-8*e*), 3.63 (dd, 1 H, $J_{1',2}$ 4.2, $J_{1,1'}$ 12.7 Hz, H-1'), 3.45 (ddd, 1 H, H-2), 3.31 (d, 1 H, $J_{2,3}$ 2.2 Hz, H-3), 1.80 (bs, 1 H, OH), 1.52, 1.46, 1.40, and 1.32 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 109.12 and 108.12 (2 CMe_2), 102.41 (C-4), 70.81, 69.90, and 68.85 (C-5,6,7), 61.16 and 60.76 (C-1,8), 56.34 and 55.71 (C-2,3), 26.36, 25.74, 25.32, and 24.14 (2 CMe_2). Mass spectrum (LSIMS): *m/z* 287.11358 (M^+-Me). For $C_{13}H_{19}O_7$ 287.1138 (deviation -1.8 ppm).

2-Deoxy-4,5:6,7-di-*O*-isopropylidene-β-D-*gluco*-oct-4-ulo-4,8-pyranose 13: To a stirred and cooled (ice-water) solution of **12** (2.41 g, 8 mmol) in dry THF (20 mL), 3.5*M* Red-Al in toluene (2.5 mL) was added dropwise under argon. The mixture was allowed to reach room temperature and then left for 2 h. GLC (*B*) then revealed the presence of two new compounds [T_R 9.37 (9.7%) and 10.48 (84.5%)]. THe excess of hydride was coutiously destroyed by addition of ether saturated with water, water and then aqueous 5% hydrochloric acid. The mixture was concentrated, extracted with ethyl acetate and the solvent was evaporated. Column chromatography (2:1 ether-hexane → ether → 10:1 ether-methanol) of the residue afforded first a mixture (0.5 g) of both compound. Eluted second was pure **13** (1.45 g, 60%), $[\alpha]_D^{24}$ -25 (c, 1.3); ν_{max}^{film}3480 (OH), 1384 and 1376 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.58 (dd, 1 H, $J_{5,6}$ 2.5, $J_{6,7}$ 7.8 Hz, H-6), 4.34 (d, 1 H, H-5), 4.22 (dd, 1 H, H-7), 3.86 (dd, 1 H, $J_{7,8a}$ 2, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.84-3.76 (m, 3 H, H-1,1',3), 3.77 (d, 1 H, H-8*e*), 2.66 (s, 2 H, HO-1,3), 1.93 (bq, 2 H, H-2,2), 1.52, 1.50, 1.36, and 1.35 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 109.37 and 108.63 (2 CMe_2), 104.32 (C-4), 75.46 (C-5), 72.86 (C-6), 70.71 and 69.98 (C-3,7), 61.38 and 61.11 (C-1,8), 32.80 (C-2), 26.35, 25.61, 25.37, and 23.93 (2 CMe_2). Mass spectrum (LSIMS): *m/z* 289.12886 (M^+-Me). For $C_{13}H_{21}O_7$ 289.12873 (deviation -0.4 ppm).

2-Deoxy-4,5:6,7-di-*O*-isopropylidene-1,3-di-*O*-methyl-β-D-*gluco*-oct-4-ulo-4,8-pyranose 14: To a stirred solution of **13** (190 mg, 0.62 mmol) in dry THF (5 mL), imidazole (50 mg), and NaH (80% oil dispersion) (60 mg, 2 mmol), were added. After 30 min, iodomethane (0.15 mL, 2.7 mmol) was added and the mixture stirred for additional 30 min. TLC (ether) then showed a faster-running product. After work-up and column chromatography (1:2 ether-hexane) of the residue afforded **14** (185 mg, 89%), $[\alpha]_D^{26}$: -35 (c 0.8); ν_{max}^{film}1383 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.41 (dd, 1 H, $J_{5,6}$ 2.2, $J_{6,7}$ 8.1 Hz, H-6), 4.32 (d, 1 H, H-5), 4.18 (ddd, 1 H, H-7), 3.87 (dd, 1 H, $J_{7,8a}$ 2, $J_{8a,8e}$ 13.2 Hz, H-8*a*), 3.75 (dd, 1 H, $J_{7,8e}$ 1.8 Hz, H-8*e*), 3.55-3.43 (m, 2 H, H-1,1'), 3.47 and 3.31 (2 s, 6 H, 2 OMe), 3.40 (dd, 1 H, $J_{2,3}$ 3, $J_{2',3}$ 10.6 Hz, H-3), 2.02 (dddd, 1 H, $J_{2,2'}$ 15.5 Hz, H-2), 1.65 (dddd, 1 H, H-2'), 1.51, 1.46, 1.43, and 1.30 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 108.62 and 107.88 (2 CMe_2), 106.34 (C-4), 79.85, 70.60, 70.45, and 70.19 (C-3,5,6,7), 69.57 (C-1), 61.26 and 58.34 (2 OMe), 60.60 (C-8), 31.91 (C-2), 26.85, 25.32, 25.30, and 23.54 (2 CMe_2). Anal. Calcd. for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49. Found: C, 57.68; H, 8.39.

Degradation of 14 to 16: A solution of **14** (1.31 g, 3.94 mmol) in aqueous 70% trifluoroacetic acid (15 mL) was left at room temperature for 2 days. TLC (ether) then showed the presence of a non mobile compound. The mixture was concentrated and repeatly codistilled with water and the residue chromatographed (10:1 chloroform-methanol) to afford a colourless solid foam (800 mg), presumably 2-deoxy-1,3-di-*O*-methyl-D-gluco-oct-4-ulose (**15**) that was not futher characterized but reduzed with $NaBH_4$ (200 mg) in methanol (10 mL). The mixture was neutralized with acetic acid and concentrated, then oxidized in water (15 mL) with a solution of $NaIO_4$ (3.15 g, 14.7 mmol) in the same solvent (35 mL). The reaction was monitorized by polarimetry to a constant rotation and then $NaBH_4$ (300 mg) was added. The mixture was saturated with NaCl, extracted with ethyl acetate, and concentrated. The residue was methylated in THF (4 mL) with NaH (50 mg), imidazole (30 mg) and yodomethane (0.3 mL) as above. Usual work-up and column chromatography (1:3 ether-hexane → ether) allowed the isolation and identification of (*S*)-1,2,4-trimetoxybutane (20 mg); $[\alpha]_D^{23}$: -8 (c 0.12), identified by comparison of its polarimetric and spectroscopic data with those of an authentic sample (see below).

(*S*)-1,2-*O*-Isopropylidene-but-3-ene-1,2-diol 18: To a stirred and cooled (ice-water) solution of potassium *tert*-butoxide (6.5 g, 58.3 mmol) in dry THF (80 mL), methyltryphenylphosphonium bromide (21 g, 58.8 mmol) was added under argon. After 1.5 h, a solution of 2,3-*O*-isopropylidene-D-gliceraldehyde (7.5 g, 57.7 mmol) in anhydrous ether (30 mL) was added and the stirring continued for 3 h. The reaction was quenched with ether saturated with water and water. The organic phase separated and washed with brine, then concentrated. From the residue distilled **18**, $b.p._{.50\,mm}$ 50 °C, $[\alpha]_D^{23}$: +32 (c, 1.2); ν_{max}^{film}1381 and 1372 cm^{-1} (CMe_2). NMR data: ^1H, δ 5.80 (ddd, 1 H, $J_{2,3}$ 7.2, $J_{3,4}$ 10.3, $J_{3,4'}$ 17.3 Hz, H-3), 5.34 (bd, 1 H, H-4), 5.18 (bd, 1 H, H-4'), 4.47 (q, 1 H, H-2), 4.07 (m, 1 H, H-1), 3.57 (t, 1 H, H-1'), 1.40 and 1.36 (2 s, 6 H, CMe_2); ^{13}C, δ 135.98 (C-3), 118.00 (C-4), 109.41 (*C*Me_2), 77.43 (C-2), 69.35 (C-1), 26.69 and 25.91 (C*Me*$_2$).

(*S*)-1,2-*O*-Isopropylidene-1,2,4-butanetriol 19: To a stirred and cooled (acetone-solid CO_2) solution of **18** (1.9 g, 14.8 mmol) in anhydrous ether (20 mL), was added dropwise under argon, 10*M* BH_3-DMS (2 mL, 20 mmol). The mixture was stirred for 30 min and then for 4 h at room temperature. 3*M* NaOH (20 mL) and aqueous 30% H_2O_2 (20 mL) were added dropwise to the stirred and ice cooled mixture. Stirring was continued overnight at room temperature, ether was added, the organic phase was separated, and the aqueous phase was extracted with ether. The combined extracts were washed with brine and water, and concentrated. Column chromatography (1:2 ether-hexane → ether) of the residue gave **19** (880 mg, 41%) as an uncolourless oil,

$[\alpha]_D^{25}$: +1.7 (c 1.2), $[\alpha]_{405}^{25}$: +7.3 (c 1.2); ν_{max}^{film}3435 (OH), 1380 and 1372 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.24 (m, 1 H, H-2), 4.06 (dd, 1 H, $J_{1,1'}$ 8, $J_{1,2}$ 6 Hz, H-1), 3.76 (bt, 2 H, H-4,4'), 3.56 (dd, 1 H, $J_{1',2}$ 7.3 Hz, H-1'), 2.50 (bs, 1 H, HO), 1.80 (bq, 2 H, H-3,3'), 1.39 and 1.32 (2 s, 6 H, CMe_2); ^{13}C, δ 109.09 (*C*Me_2), 74.99 (C-2), 69.50 (C-1), 60.44 (C-4), 35.76 (C-3), 26.92 and 25.71 (C*Me*$_2$).

(*S*)-1,2-*O*-Isopropylidene-4-*O*-methyl-1,2,4-butanetriol 20: Compound **19** (800 mg, 5.48 mmol) was methylated in dry THF (15 mL) with potassium *tert*-butoxide (750 mg, 6.7 mmol) and yodomethane (1 mL) as above. After

usual work-up and column chromatography (1:1 ether-hexane) of the residue gave **20** (640 mg, 73%) as an uncolourless oil, $[\alpha]_D^{23}$: +6 (c 1.1); ν_{max}^{film}1380 and 1371 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.15 (m, 1 H, H-2), 4.03 (dd, 1 H, $J_{1,1'}$ 8, $J_{1,2}$ 6 Hz, H-1), 3.52 (t, 1 H, $J_{1',2}$ 8 Hz, H-1'), 3.46-3.41 (m, 2 H, H-4,4'), 3.30 (s, 3 H, OMe), 1.91-171 (m, 2 H, H-3,3'), 1.37 and 1.32 (2 s, 6 H, CMe_2); ^{13}C, δ 108.63 (*C*Me_2), 73.81 (C-2), 69.65 and 69.47 (C-1,4), 58.76 (OMe), 35.83 (C-3), 26.98 and 25.81 (C*Me*$_2$). Mass spectrum (c.i. CH_4): ***m/z*** 161 (1.3%, M^++1), 159 (3.2, M^+-1), 145 (22.0, M^++1-CH_4), 103 (100.0, M^++1-Me_2CO), and 71 (81.8, M^++1-Me_2CO-MeOH).

(*S*)-1,2,4-Tri-*O*-methyl-1,2,4-butanetriol 16: A solution of **20** (640 mg, 4 mmol) and *p*-toluenesulfonic acid (50 mg) in methanol (5 mL) was maintained at room temperature for 30 min. TLC (ether) then revealed a non mobile compound. The mixture was neutralized (solid K_2CO_3), filtered and the filtrate concentrated. The residue was extracted with ethyl acetate (20 mL) and then concentrated to a residue (400 mg) that was subsequently methylated in dry THF (10 mL) with NaH (80% oil dispersion) (300 mg, 10 mmol), imidazole (100 mg), and yodomethane (0.6 mL, 10 mmol) as above. After usual work-up and column chromatography (1:3 ether-hexane) pure **16** (120 mg, 30%) was obtained as an uncolourless oil, $[\alpha]_D^{25}$: -10, $[\alpha]_{405}^{25}$: -22 (c 1.3); ν_{max}^{film}1119 cm^{-1} (C-O-C). NMR data: ^1H, δ 3.48-3.32 (m, 5 H, H-1,1',2,4,4'), 3.38, 3.34, and 3.30 (3 s, 9 H, 3 OMe), and 1.74 (q, 2 H, J 6.3 Hz, H-3,3); ^{13}C, δ 77.11 (C-2), 74.45 (C-1), 68.94 (C-4), 59.00, 58.36, and 57.41 (3 OMe), and 31.13 (C-3). Mass spectrum: ***m/z*** 149 (0.5%, M^++1), 148 (18.9, M^+), 116 (2.7, M^+-MeOH), 104 (3.2, M^++1-C_2H_5O), 103 (66.5, M^+-C_2H_5O), 45 (100, $C_2H_5O^+$). Anal. Calcd. for $C_7H_{16}O_3$: C, 56.73; H, 10.88. Found: C, 56.81; H, 11.02.

4,5:6,7-Di-*O*-isopropylidene-β-D-*arabino*-D-erythro-oct-4-ulo-4,8-pyranose 22: A solution of compound **12** (260 mg, 0.86 mmol) in 0.5*M* sodium hydroxide (5 mL) containing 1,4-dioxane (2 mL) was heated at 70° for 24 h and then at room temperature for further 24 h. TLC (ether) then revealed the presence of a non mobile compound. The mixture was neutralized with acetic acid, concentrated and the residue extracted with ethyl acetate. Concentration of the extracts followed by column chromatography of the residue (ethyl acetate) gave syrupy **22** (100 mg, 37%), $[\alpha]_D^{26}$: -15 (c 0.6); ν_{max}^{film}3468 (OH) and 1386 cm^{-1} (CMe_2). NMR data (400 MHz): ^1H, δ 4.59 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,7}$ 7.9 Hz, H-6), 4.41 (d, 1 H, H-5), 4.23 (bdd, 1 H, H-7), 4.00 (dt, 1 H, $J_{1,2}$ 4 Hz, H-2), 3.87 (dd, 1 H, $J_{7,8a}$ 2, $J_{8a,8e}$ 13 Hz, H-8a), 3.82-3.75 (m, 3 H, H-1,1',8*e*), 3.61 (d, 1 H, $J_{2,3}$ 7.8 Hz, H-3), 2.52 (bs, 3 H, HO-1,2,3), 1.53, 1.51, 1.40, and 1.35 (4 s, 12 H, 2 CMe_2); ^{13}C, δ 109.51 and 109.37 (2 *C*Me_2), 104.90 (C-4), 74.93, 72.85, 70.63, 70.50, and 69.70 (C-2,3,5,6,7), 63.94 and 61.13 (C-1,8), 26.22, 25.36, 25.27, and 23.79 (2 C*Me*$_2$). Mass spectrum (LSIMS): ***m/z*** 305.12419 (M^+-Me). For $C_{13}H_{21}O_8$ 305.12364 (deviation -1.8 ppm).

4,5:6,7-Di-*O*-isopropylidene-1,2,3-tri-*O*-methyl-β-D-*arabino*-D-*erythro*-oct-4-ulo-4,8-pyranose 23: Compound **22** (100 mg, 0.3 mmol) in dry Me_2SO (3 mL) was methylated with NaH (80% oil dispersion) (90 mg, 3 mmol), imidazole (50 mg) and yodomethane (1 mL) as compound **4**, Conventional work-up and column chromatography (1:2 ether-hexane) of the residue afforded syrupy **23** (75 mg, 70%), $[\alpha]_D^{24}$: -40 (c 1.3); ν_{max}^{film}1383 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.49 (dd, 1 H, $J_{5,6}$ 2.3, $J_{6,7}$ 8.1 Hz, H-6), 4.34 (d, 1 H, H-5), 4.18 (bdd, 1 H, H-7), 3.87

(dd, 1 H, $J_{7,8a}$ 2.1, $J_{8a,8e}$ 13 Hz, H-8*a*), 3.76 (bd, 1 H, H-8*e*), 3.75 (dt, 1 H, H-2), 3.61 (dd, 1 H, $J_{1,2}$ 2, $J_{1,1'}$ 10.6 Hz, H-1), 3.54 (d, 1 H, $J_{2,3}$ 1.7 Hz, H-3), 3.45 (dd, 1 H, $J_{1',2}$ 8.1 Hz, H-1'), 3.51, 3.40 and 3.33 (3 s, 9 H, 3 OMe), 1.50, 1.38, and 1.31 (3 s, 12 H, 2 CMe_2); ^{13}C, δ 108.96 and 107.87 (2 CMe_2), 104.66 (C-4), 84.20 (C-3), 81.44 (C-2), 72.84 (C-1), 70.72, 70.53, and 70.37 (C-5,6,7), 60.96 (C-8), 61.86, 59.04 and 57.43 (3 OMe), 26.65, 25.58, 25.33, and 23.79 (2 CMe_2). Mass spectrum (LSIMS): *m/z* 362.19417 (M^+). For $C_{17}H_{30}O_8$ 362.19407 (deviation -0.3 ppm).

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