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Note

A synthesis of L-*galacto*-D-*galacto*-decose*

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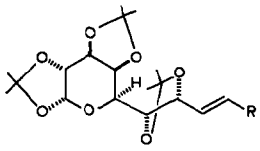
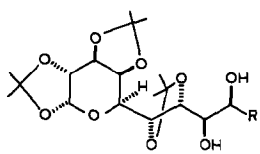
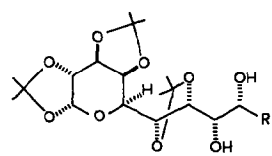
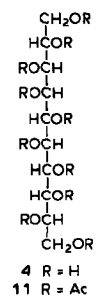
In earlier work[2], the OsO_4-catalysed *cis*-hydroxylation of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**1**) was shown to produce a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**2**) and the α-D-*ido*-D-*galacto* isomer **3** in the ratio ~2.5:1. Acid hydrolysis of the mixture of **2** and **3** followed by reduction of the resulting decoses permitted the isolation of crystalline L-*galacto*-D-*galacto*-decitol (**4**), although we were unable to isolate the parent decose **5** after the hydrolysis step. Whilst the prospect of obtaining **5** would be greatly enhanced if **2** could be obtained in pure form, all attempts to separate **2** from **3** by chromatography were unsuccessful.

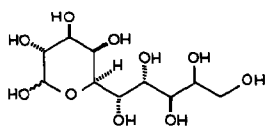
Although the stereoselectivity for the osmylation of **1** is modest, the prevail-

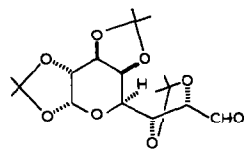


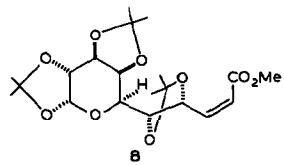












*Higher-carbon sugars, Part 4. For Part 3, see ref. 1.
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ing isomer is the one predicted by Kishi's empirical rule for osmylation[3], which states that the relative stereochemistry between the pre-existing hydroxyl or alkoxyl group and the adjacent, newly introduced hydroxyl group of the major product is *erythro*. The stereoselectivity observed in osmylation reactions has been rationalised on stereoelectronic grounds[4]. Since notable exceptions to Kishi's empirical rule are found with conjugate esters[3,5], the stereoselectivities for the catalytic osmylation of methyl (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranuronate (**7**) and the corresponding (*Z*)-isomer **8** are of theoretical and, possibly, practical interest.

Treatment of a methanolic solution of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-octodialdo-1,5-pyranose[2] (**6**) with (methoxycarbonylmethylene)triphenylphosphorane[6] furnished a mixture of **7** and **8** in the ratio ~5:4. Crystallisation from hexane provided the (*Z*)-enopyranuronate **8**, while the mother liquor contained the (*E*)-enopyranuronate **7** in essentially pure form. The stereochemistry of **7** followed from its conversion into **1**[2,7] on reduction with lithium aluminium hydride. Catalytic osmylation[8] of **7** produced a mixture of 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranuronate (**9**) and the α-D-*ido*-D-*galacto* isomer **10**, which were obtained in the ratio ~5:3, respectively, following preparative chromatography. The slight preference in the osmylation reaction for the product predicted by Kishi's empirical rule was revealed by reduction of **9** to **2**[2] (identified by ^{1}H-n.m.r. spectroscopy). This route furnished **2** in a chromatographically pure form, and subsequently yielded L-*galacto*-D-*galacto*-decose (**5**), isolated as the crystalline monohydrate, on hydrolysis of **2** with aqueous trifluoroacetic acid. The identity of **5** was confirmed by its conversion into L-*galacto*-D-*galacto*-decitol[2,7] (**4**)* on reduction. We also took the opportunity to characterise **4** as the crystalline deca-acetate **11**.

The OsO_4-catalysed *cis*-hydroxylation of the (*Z*)-enopyranuronate **8** turned out to be of no practical use, since the hydroxylated products (ratio, 1.5:1; determined by 360-MHz ^{1}H-n.m.r. spectroscopy) could not be separated or identified. Moreover, this reaction, like the comparable reaction with **7**, exhibits only a modest stereoselectivity.

The only other known decose was synthesised[9] from D-glucose in 1912, using the Fischer–Kiliani cyanohydrin method to ascend the series. By invoking Maltby's generalisation[10], it was later suggested[11] that this decose is probably D-*gluco*-D-*galacto*-decose, although it remains for this structure to be rigorously established.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. ^{1}H-N.m.r. spectra were recorded for solutions in deuteriochloroform (internal Me_4Si) with a Bruker Spectrospin (90 MHz) spectro-

*The decitol **4** is readily identifiable, by virtue of its C_2 symmetry, using ^{13}C-n.m.r. spectroscopy[2].

meter. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Melting points are uncorrected.

Methyl (E)- *and* (Z)-*8,9-dideoxy-1,2:3,4:6,7-tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec-8-enopyranuronate* (**7** *and* **8**). — (Methoxycarbonylmethylene)triphenylphosphorane[6] (2.7 g, 8.1 mmol) was added gradually to a cooled (0°) solution of **6**[2] (2.53 g, 7.05 mmol) in anhydrous methanol (46 mL), and the mixture was stirred at 0° for 2 h and then concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 20:1 dichloromethane–acetone) gave a mixture (~2.7 g) of **7** and **8**. Crystallisation from hexane gave the (*Z*)-isomer **8** (1.2 g, 41%), m.p. and mixture m.p. 134.5–136°; lit.[7] m.p. 134.5–136°. Concentration of the mother liquor provided the (*E*)-isomer **7** (1.49 g, 51%), $[\alpha]_D$ ~−45.5° (*c* 1, chloroform), as an essentially pure syrup. ^{1}H-N.m.r. data *(inter alia):* δ 7.07 (dd, 1 H, $J_{8,9}$ 15, $J_{7,8}$ 4.5 Hz, H-8), 6.16 (dd, 1 H, $J_{7,9}$ ~1 Hz, H-9), 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.74 (s, 3 H, CO_2Me), and 1.52, 1.44, and 1.32 (3 s, ratios 1:3:2, 18 H, 3 CMe_2).

Catalytic osmylation of methyl (E)-*8,9-dideoxy-1,2:3,4:6,7-tri*-O-*isopropylidene*-α-D-threo-D-galacto-*dec-8-enopyranuronate* (**7**). — A solution of **7** (1 g, 2.4 mmol) in acetone–water (8:1, 18 mL) containing *N*-methylmorpholine *N*-oxide monohydrate (0.65 g, 4.8 mmol) and osmium tetraoxide (0.04 g, 0.16 mmol) was stirred at room temperature for 16 h prior to work-up in the usual manner[1]. Chromatography of the residue on silica gel (elution with 4:1 dichloromethane–acetone) gave, first, methyl 1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranuronate (**9**; 0.556 g, 51%), $[\alpha]_D$ −55° (*c* 1.2, chloroform), as a syrup (Found: C, 53.9; H, 7.0. $C_{20}H_{32}O_{11}$ calc.: C, 53.6; H, 7.2%). ^{1}H-N.m.r. data *(inter alia):* δ 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.81 (s, 3 H, CO_2Me), and 1.51, 1.47, 1.44, and 1.33 (4 s, ratios 1:1:2:2, 18 H, 3 CMe_2). Continued elution gave methyl 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*ido*-D-*galacto*-decopyranuronate (**10**; 0.342 g, ~32%), contaminated with traces of **9** and other impurities.

L-galacto-D-galacto-*Decose* (**5**). — Lithium aluminium hydride (0.1 g, ~2.6 mmol) was added gradually to a solution of **9** (0.193 g, 0.43 mmol) in anhydrous tetrahydrofuran (8 mL), and the reaction mixture was stirred for 4 h at room temperature prior to the decomposition of the excess of the reagent with wet ethyl acetate. Inorganic material was filtered off and washed thoroughly with ethyl acetate, and the filtrate and washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 1:1 dichloromethane–acetone) gave **2** (0.12 g, 66%), $[\alpha]_D$ −43° (*c* 1.1, chloroform), as a syrup. ^{1}H-N.m.r. data *(inter alia):* δ 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), and 1.52, 1.47, 1.43, and 1.33 (4 s, ratios 1:1:2:2, 18 H, 3 CMe_2).

A solution of **2** (0.346 g, 0.82 mmol) in trifluoroacetic acid–water (9:1, 7 mL) was kept for 20 min at room temperature prior to concentration under reduced pressure with occasional additions of water. The resulting solid was recrystallised from aqueous ethanol to give **5** as the monohydrate (0.152 g, 58%), m.p. 148–150°, $[\alpha]_D$ +28° (10 min)→+40° (final; *c* 1, water) (Found: C, 37.9; H, 6.8. $C_{10}H_{20}O_{10} \cdot H_2O$ calc.: C, 37.7; H, 7.0%).

Reduction of **5** with sodium borohydride in aqueous solution, as previously described[2,7], afforded L-*galacto*-D-*galacto*-decitol (**4**), m.p. and mixture m.p. 224–226°; lit.[2] m.p. 224.5–226°.

L-galacto-D-galacto-*Decitol deca-acetate* (**11**). — A suspension of **4** (0.045 g, 0.15 mmol) in anhydrous pyridine (4 mL) and acetic anhydride (2 mL) was heated and stirred at 100° for 3 h. After cooling, the clear solution was poured into ice–water, the aqueous solution was extracted with chloroform, and the extract was washed with dilute hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). The solid obtained on removal of the solvent was recrystallised several times from aqueous ethanol to give **11** (0.095 g, 88%), m.p. 196–197°, $[\alpha]_D$ −3° (*c* 1, chloroform) (Found: C, 49.6; H, 5.6. $C_{30}H_{42}O_{20}$ calc.: C, 49.9; H, 5.9%). The 90.5-MHz ^{13}C-n.m.r. spectrum of **11** in deuteriochloroform exhibited resonances at δ 170.23, 170.19, and 169.55 (C=O groups), 67.52, 67.47, 67.10, 66.72, and 62.11 (chain carbon atoms), and 20.46, 20.32, and 20.25 (CH_3 groups).

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