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Preliminary communication

Higher-carbon sugars: the synthesis of some decitols *via* the epoxide route

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Since so few higher-carbon sugars are known[1], the problem of characterising them cannot be tackled in the same way as with lower members of the series (for example, the pentoses and hexoses and their derivatives). It is imperative, therefore, in the synthesis of higher-carbon sugars to employ reactions whose stereo- and regio-chemistry can be predicted with reasonable certainty, so that identification of the products does not become burdensome. Catalytic osmylation of unsaturated seven-[2], eight-[3], and ten-carbon sugars[4] generally affords products of predictable stereochemistry, except for (*Z*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*threo*-D-*galacto*-dec-8-enopyranose (**1**) which gave[4] equal proportions of 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*altro*-D-*galacto*-decopyranose (**2**), the isomer expected to preponderate[5], and the β-L-*gluco*-D-*galacto* isomer **3**. The lack of stereoselectivity of the latter reaction was not only detrimental from a synthetic viewpoint, but also precluded a tentative assignment of structure to the individual isomers on the basis of Kishi's empirical rule[5]. Consequently, we sought an alternative route to **2** and **3** *via* Sharpless epoxidation[6] of the equally accessible[4] (*E*)-decenopyranose derivative **4**. The stereochemistry of asymmetric epoxidation of **4** can be predicted from the Sharpless model[6]**, while the regiochemistry of base-catalysed opening of the resulting epoxy alcohols, involving epoxide-migration (Payne rearrangement[7]), should also follow a predictable course[6,8].

Sharpless epoxidation[6] of **4** at –23° with di-isopropyl L-(+)-tartrate as the chiral ligand furnished a mixture of 8,9-anhydro-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*galacto*-D-*galacto*-decopyranose (**5**; isolated in 63% yield), m.p. 128–128.5° (from ether–hexane), $[\alpha]_D$ –58° (*c* 0.9, chloroform), and the α-D-*ido*-D-*galacto* isomer **6** in the ratio ~5:1. The structure assigned to the preponderant epoxide **5** on the basis of the Sharpless model[6] was placed on a secure footing when similar epoxidation of **4** with di-isopropyl D-(–)-tartrate as the chiral ligand yielded a mixture (71%) in which the isomeric epoxide **6** preponderated (ratio **6**/**5** ~4:1). Hydrolysis of **5** with sodium hydroxide in aqueous 1,4-dioxane at 70° yielded **2** (63%), $[\alpha]_D$ –50° (*c* 1.3, chloroform), which, by analogy[6,8], was considered to be formed by preferential opening of the epoxide

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This requires the diastereofacial selectivity of the chiral epoxidising reagent to be large enough to outweigh that of the chiral substrate **4, so that the reaction is reagent controlled.

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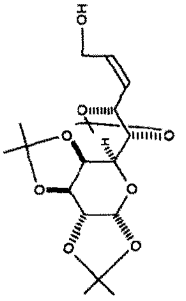

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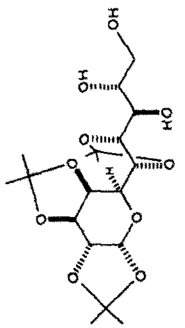

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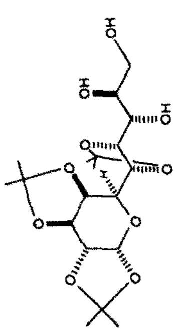

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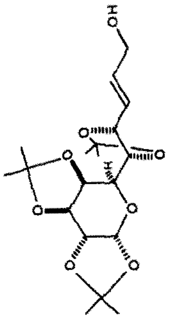

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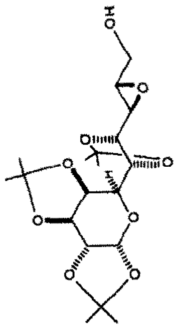

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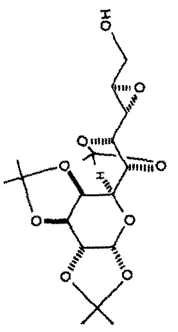

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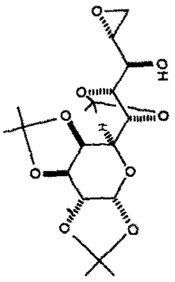

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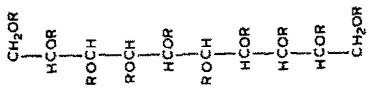

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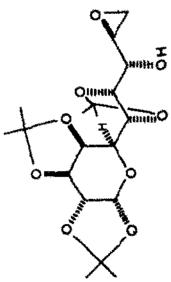
9 R = Ac



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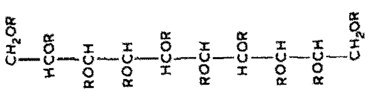
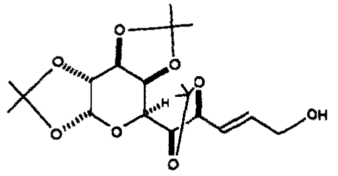


11 R = H
12 R = Ac

7 (the product of a Payne rearrangement[7] of 5 *in situ*) at the terminal position with hydroxide ion. Acid hydrolysis (CF_3CO_2H–H_2O) of 2 and reduction ($NaBH_4$) of the resulting decose gave D-*altro*-D-*galacto*-decitol (8; 92%), $[\alpha]_D$ ~+0.6° (*c* 2.3, water), which, on acetylation (Ac_2O in pyridine at 100°), afforded the deca-acetate 9 (73%), $[\alpha]_D$ +27° (*c* 1.3, chloroform). Although neither 8 nor 9 were crystalline, their analytical data and/or spectroscopic properties were entirely consistent with the structures assigned*.

Hydrolysis of a 4:1 mixture of the epoxy alcohols 6 and 5 with sodium hydroxide in aqueous 1,4-dioxane at 70° provided a mixture (51%) containing the triols 3 and 2 (ratio 4:1), which were presumably derived from preferential opening of the respective Payne-rearrangement[7] products **10** and 7 at the terminal position. Acid hydrolysis) CF_3CO_2H–H_2O) of a mixture enriched in 3 and reduction ($NaBH_4$) of the liberated decose then gave L-*gluco*-D-*galacto*-decitol (**11**)**, m.p. 155–156.5° (from aqueous ethanol), $[\alpha]_D$ $-2°$ (*c* 1, water), in 37% yield. Acetylation (Ac_2O in pyridine at 100°) of **11** furnished the deca-acetate **12** (71%), m.p. 139–141° (from ether–hexane), $[\alpha]_D$ $-23°$ (*c* 1, chloroform).

In related work, Sharpless epoxidation[6] of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-β-L-*threo*-D-*galacto*-dec-8-enopyranose[4] (**13**; prepared from D-galactose) with di-isopropyl L-(+)-tartrate as the chiral ligand provided **14** as the preponderant epoxy alcohol (isomer ratio ~4:1), which was transformed, *via* **15** and **16**, into D-*gluco*-D-*galacto*-decitol (**17**), m.p. 217–219° (from aqueous ethanol), $[\alpha]_D$ + 1° (saturated solution, water); lit.[9] m.p. 222°, $[\alpha]_D$ +1.2° (water). Acetylation of **17** gave the deca-acetate **18**, m.p. 149–150° (from ether–hexane), $[\alpha]_D$ +15.5° (*c* 1, chloroform); lit.[9] m.p. 149–150°, $[\alpha]_D$ + 16° (*c* 5, chloroform). D-*gluco*-D-*galacto*-Decitol (**17**) was



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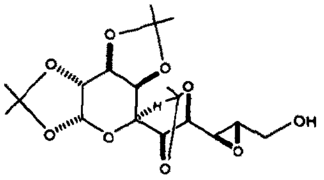

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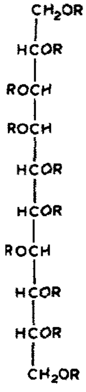
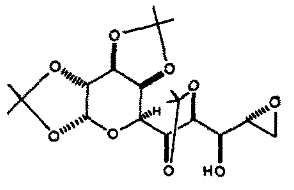


17 R = H

18 R = Ac



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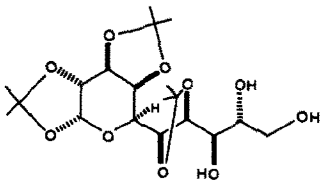

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*The ^{13}C-n.m.r. (90 MHz) spectrum of 8 in $(CD_3)_2SO$ exhibited ten resonances, of roughly equal intensity, at δ 73.24, 71.84, 71.37, 70.79, 70.07, 69.92, 69.68, 69.38, 63.22, and 62.84, while the ^{13}C- and ^1H-n.m.r. (360 MHz) spectra of 9 in $CDCl_3$ clearly indicated the presence of ten acetate groups.

**For a solution of 11 in $(CD_3)_2SO$, the resonances in the ^{13}C-n.m.r. spectrum appeared at δ 75.24, 72.77, 71.49, 71.39, 70.03, 69.45, 68.74, 68.68, 63.53, and 63.35.

derived originally from D-glucose by successive applications of the cyanohydrin procedure[9], although rigorous proof of its structure has never been provided[1]. The foregoing synthesis of D-*gluco*-D-*galacto*-decitol (**17**) from D-galactose, in conjunction with that from D-glucose[9], establishes the configuration at all eight stereocentres, and finally settles the structure of this decitol.

New compounds had elemental analyses and/or spectroscopic properties in agreement with the structures assigned.

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