Carbohydrate Research, 140 (1985) C9–C12
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Preliminary communication

Higher-carbon sugars: a synthesis of L-*galacto*-D-*galacto*-decitol and related studies

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(Received April 27th, 1985; accepted for publication, May 10th, 1985)

Few higher-carbon sugars containing eight or more carbon atoms are known[1,2]; they include one decitol, probably D-*gluco*-D-*galacto*-decitol[1], synthesised from D-glucose over seventy years ago[3]. We recently synthesised a number of octose derivatives *via* the stereoselective osmylation of unsaturated precursors (*e.g.*, 1→2)[4]. By adopting an iterative approach, further extension of the sugar chain by two carbon atoms, yielding decose derivatives, should be possible. We illustrate this approach by a synthesis of L-*galacto*-D-*galacto*-decitol (**14**), which is readily identifiable by virtue of its C_2-symmetry.

As noted previously[4], catalytic osmylation of methyl (*Z*)-6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-oct-6-enopyranuronate (**3**) produces a mixture of methyl 1,2:3,4-di-*O*-isopropylidene-L-*erythro*-α-D-*galacto*-octopyranuronate (**4**) and the D-*erythro*-α-D-*galacto* isomer **5** in the ratio 4:1. Following acetonation of the mixture of **4** and **5** with 2-methoxypropene in dichloromethane containing a catalytic amount of toluene-*p*-sulphonic acid, methyl 1,2:3,4:6,7-tri-*O*-isopropylidene-L-*erythro*-α-D-*galacto*-octopyranuronate (**6**), m.p. 130.5–131.5°, $[\alpha]_D$ −81° (*c* 1.1, chloroform), was isolated in >40% yield by crystallisation from hexane. Reduction of **6** in tetrahydrofuran with lithium aluminium hydride at room temperature then gave 1,2:3,4:6,7-tri-*O*-isopropylidene-L-*erythro*-α-D-*galacto*-octopyranose (**7**, 88%), m.p. 99–100.5° [from ethyl acetate–light petroleum (b.p. 40–60°)], $[\alpha]_D$ −91° (*c* 1, chloroform). On oxidation with pyridinium chlorochromate[5], **7** afforded the 8-aldehydo derivative **8**, which, without extensive purification, was epimerised at C-7 (potassium carbonate in methanol[6]) to give 1,2:3,4:6,7-tri-*O*-isopropylidene-D-*threo*-α-D-*galacto*-octodialdo-1,5-pyranose (**9**, 58% overall), $[\alpha]_D$ ~−55° (*c* 1.7, chloroform).

The reaction between **9** and formylmethylenetriphenylphosphorane[7] in refluxing benzene furnished the (*E*)-enal **10** (91%), $[\alpha]_D$ −45° (*c* 1, chloroform), which, on reduction with di-isobutylaluminium hydride in dichloromethane at 0°, afforded (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-D-*threo*-α-D-*galacto*-dec-8-enopyranose (**11**, 63%), $[\alpha]_D$ −45° (*c* 1.2, chloroform). Catalytic osmylation[8] of **11** produced a mixture (74%) of 1,2:3,4:6,7-tri-*O*-isopropylidene-L-*galacto*-α-D-*galacto*-decopyranose (**12**) and the D-*ido*-α-D-*galacto* isomer **13** in the ratio ~2.5:1. The identity of the major stereoisomer **12** was established by the isolation of L-*galacto*-D-*galacto*-decitol (**14**, 47%),

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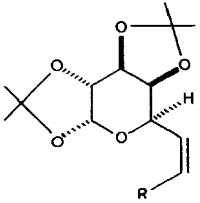

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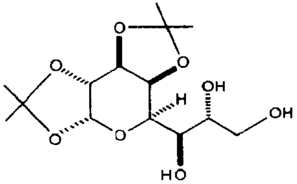
3 R = CO_2Me



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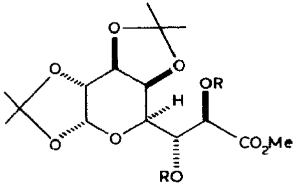
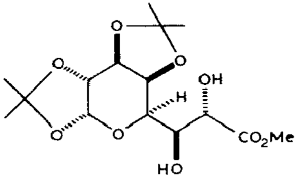


4 R = H

6 R,R = CMe_2



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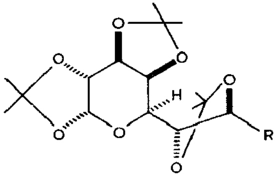
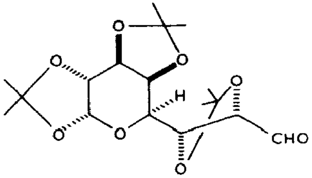


7 R = CH_2OH

8 R = CHO



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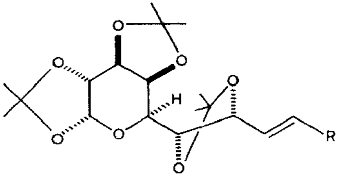
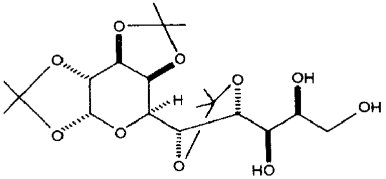


10 R = CHO

11 R = CH_2OH



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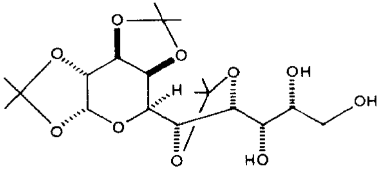

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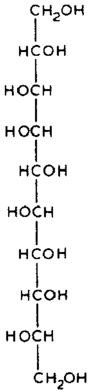

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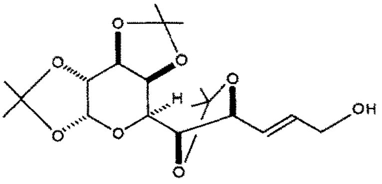
m.p. 224.5–226° (from aqueous ethanol), $[\alpha]_D$ −0.5 ±0.2° (*c* 0.8, water)†, following acid hydrolysis (CF_3CO_2H–H_2O) of the mixture of **12** and **13**, and reduction ($NaBH_4$) of the resulting decoses. In agreement with the C_2-symmetry of **14**, only five resonances, of roughly equal intensity, were observed in its ^{13}C-n.m.r. spectrum*. Although the stereoselectivity for the osmylation of **11** is fairly modest, the major isomer is the one predicted by Kishi's empirical rule for osmylation[9].



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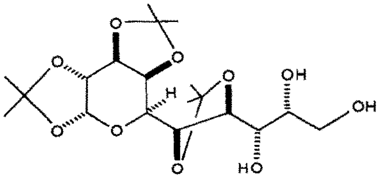

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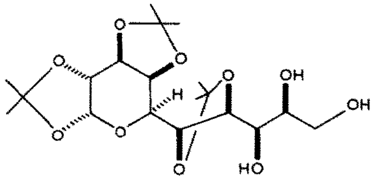

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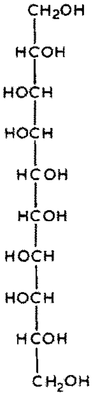

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We found also that catalytic osmylation[8] of (*E*)-8,9-dideoxy-1,2:3,4:6,7-tri-*O*-isopropylidene-L-*threo*-α-D-*galacto*-dec-8-enopyranose (**15**; obtained in six steps from **2**[4]) afforded a mixture (76%) of 1,2:3,4:6,7-tri-*O*-isopropylidene-D-*galacto*-α-D-*galacto*-decopyranose (**16**) and the L-*ido*-α-D-*galacto* isomer **17** in the ratio ~3:2. A sample of relatively pure (*meso*)-*galacto-galacto*-decitol (**18**), m.p. >280° (dec.), was obtained following acid hydrolysis (CF_3CO_2H–H_2O) of the mixture of **16** and **17**, and reduction ($NaBH_4$) of the resulting decoses. The C_s-symmetry of **18** was revealed by the appearance of only five resonances, of roughly equal intensity, in its ^{13}C-n.m.r. spectrum**.

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

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†Chiral alditols in aqueous solution invariably exhibit low $[\alpha]_D$ values[2].

*For a solution of **14** in $(CD_3)_2SO$, the resonances appeared at δ 70.40, 70.08, 70.06, 69.69, and 63.27.

For a solution of **18 in $(CD_3)_2SO$, the resonances appeared at δ 70.46, 69.77, 68.81, 68.71, and 63.34.

ACKNOWLEDGMENTS

We thank Dr. I. H. Sadler and his colleagues at Edinburgh University for the ^{13}C-n.m.r. spectra, and the Commonwealth Scholarship Commission in the United Kingdom for financial support (to A.K.M.S.K.).

REFERENCES

1 C. S. Hudson, *Adv. Carbohydr. Chem.*, 1 (1945) 1–36.

2 J. M. Webber, *Adv. Carbohydr. Chem.*, 17 (1962) 15–63; J. S. Brimacombe and J. M. Webber, in W. Pigman and D. Horton (Eds.), *The Carbohydrates: Chemistry and Biochemistry*, Vol. IA, Academic Press, New York and London, 1972, pp. 479–518.

3 L.-H. Philippe, *Ann. Chim. Phys.*, 26 (1912) 289–418.

4 J. S. Brimacombe, R. Hanna, and F. Bennett, *Carbohydr. Res.*, 135 (1985) C17–C21.

5 E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, (1975) 2647–2650.

6 A. W. M. Lee, V. S. Martin, S. Masamune, K. B. Sharpless, and F. J. Walker, *J. Am. Chem. Soc.*, 104 (1982) 3515–3516.

7 H. J. Bestmann, O. Vostrowsky, H. Paulus, W. Billmann, and W. Stransky, *Tetrahedron Lett.*, (1977) 121–124.

8 V. Van Rheenen, R. C. Kelly, and D. Y. Cha, *Tetrahedron Lett.*, (1976) 1973–1976.

9 J. K. Cha, W. J. Christ, and Y. Kishi, *Tetrahedron*, 40 (1984) 2247–2255.