Dilution-dependent Formation of a Linear (1→5)-β-D-Galactofuranan or Cyclic [(1→5)-β-D-Galactofurano]oligosaccharides

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A ten-fold decrease in the concentration of a monomer **2** switches the course of its $TrClO_4$-catalysed condensation from formation of a linear polysaccharide to that of cyclic oligosaccharides.

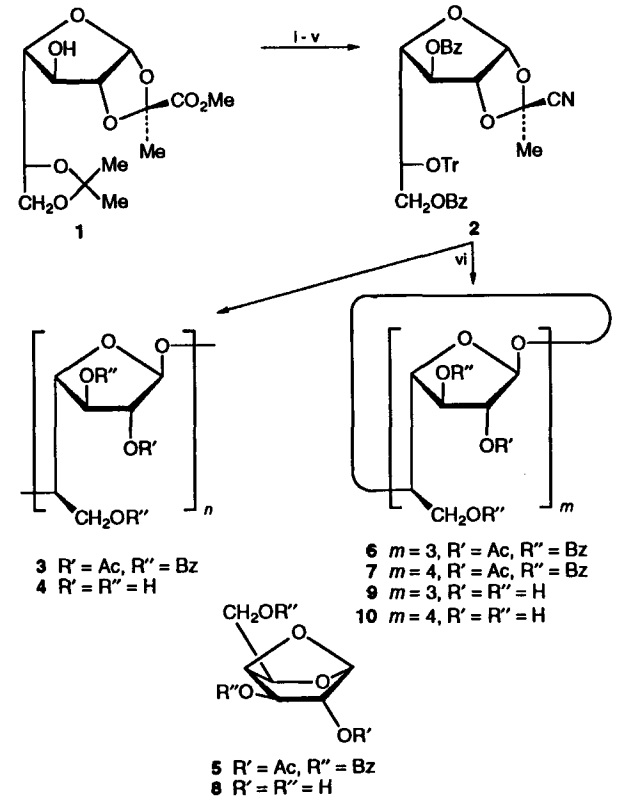
Tritylated 1,2-*O*-(1-cyanoethylidene) derivatives of mono- and oligosaccharides produce, upon $TrClO_4$-catalysed polycondensation, regular polysaccharides.[1] A characteristic feature of D-galactofuranose-derived monomers is the simultaneous formation, in this reaction, of both linear polysaccharides and cyclic oligosaccharides.[2–5] Here we report that the direction of the condensation can be dilution-dependent.

The monomer **2**,† prepared from the known [2] isopropylidene derivative **1**, afforded under 'ordinary' conditions (0.24 mol dm^{-3} in CH_2Cl_2, 0.02 mol dm^{-3} $TrClO_4$, 20 °C, 22 h) the polymeric product **3**† in 94% yield, deacylation of which gave the (1→5)-β-D-galactofuranan **4**† with molecular-mass parameters similar to those for the (1→6)-β-D-galactofuranan with DP_n (number-average degree of polymerization) of ~30 (ref. 2). On the other hand, when the reaction was carried out at the monomer concentration of 0.025 mol dm^{-3} and that of $TrClO_4$ of 0.014 mol dm^{-3} (relatively high promoter-to-monomer ratio ensured reasonable reaction rate) for 40 h at 20 °C, low-molecular products **5–7**† were obtained in 84% combined yield. They were separately deacylated into compounds **8–10**.†

That the oligosaccharides **6**, **7** (and **9**, **10**) are cyclic followed from the presence in their NMR spectra of only a single series of signals for a galactofuranose unit, which reflects their intrinsic symmetry. Convincing evidence for their cyclic nature and the cycle size was obtained from LSIMS (+)-mode.‡

Quite unexpected was the formation of the 1,5-anhydro-α-D-galactofuranose (1,4-anhydro-β-D-galactopyranose) derivative **5** though anhydridization of certain pyranose monomers is documented.[6,7]

In conclusion, we have demonstrated for the first time that linear polysaccharides or cyclic oligosaccharides (at least in the galactofuranose series) can be prepared by varying dilution conditions.



Scheme 1 *Reagents and conditions:* i, BzCl, pyridine, 20 °C, 2 h (86%); ii, $CHCl_3$–90% aq. CF_3CO_2H (1:1), 20 °C, 10 min (88%); iii, *N*-benzoylimidazole, $CHCl_3$, reflux, 24 h (73%); iv, $TrClO_4$, 2,4,6-collidine, CH_2Cl_2, 20 °C (89%); v, NH_3, $CHCl_3$–MeOH, 20 °C, 5 h, then BzCl, Py, 20 °C, 18 h (86%); vi, $TrClO_4$, CH_2Cl_2, 20 °C.

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† All compounds obtained gave satisfactory ^1H and ^{13}C NMR spectra, which were recorded with Bruker WM-250 and Bruker AM-300 instruments, respectively. All optical rotations were measured on a DIP-360 polarimeter (JASCO, Japan) in chloroform and water for protected and deprotected sugar derivatives, respectively. TLC was performed on Kieselgel-60 plates (Merck, Germany). *Characterisation data for* **2**: $[\alpha]_D^{28}$ −41 °(*c* 1.0), m.p.128–130 °C.

3, R_F 0.25–0.5 (toluene–methanol, 9:1).

4, $[\alpha]_D^{25}$ −124 ° (*c* 0.66); δ_C (D_2O) 108.2 (1–C), 82.6 (2–C), 77.65 (3–C), 82.65 (4–C), 76.8 (5–C), 62.3 (6–C).

5, $[\alpha]_D^{29}$ +100 ° (*c* 1.02); R_F 0.65 (toluene–ethyl acetate, 4:1).

6, $[\alpha]_D^{26}$ −52 ° (*c* 0.95); R_F 0.58.

7, $[\alpha]_D^{24}$ −88 ° (*c* 1.36); R_F 0.50.

8, $[\alpha]_D^{27}$ +126 ° (*c* 1.02); δ_H (D_2O) 5.59 (d, 1 H, $J_{1,2}$ 2.7 Hz, 1–H), 3.94 (ddd, 1H, $J_{2,3}$ 1.1, $J_{2,4}$ 1.9 Hz, 2–H), 3.76 (d, 1H, 3–H), 4.57 (d, 1H, 4–H), 3.82 (dd, 1H, $J_{5,6a}$ 5.2, $J_{5,6b}$ 6.0 Hz, 5–H), 3.58 (dd, 1H, $J_{6a,6b}$ 11.7 Hz, 6a–H), 3.51 (dd, 1H, 6b–H); δ_C 101.0 (1–C).

9, δ_H (D_2O) 5.14 (d, 1H, $J_{1,2}$ 2.5 Hz, 1–H), 4.10 (dd, 1H, $J_{2,3}$ 4.3 Hz, 2–H), 3.92 (dd, 1H, $J_{3,4}$ 7.4 Hz, 3–H), 4.27 (dd, 1H, $J_{4,5}$ 6.7 Hz, 4–H), 3.88 (m, 1H, $J_{5,6a}$ 3.0, $J_{5,6b}$ 7.2 Hz, 5–H), 3.82 (dd, 1H, $J_{6a,6b}$ 12.0 Hz, 6a–H), 3.69 (dd, 1H, 6b–H).

10. $[\alpha]_D^{26}$ −90 ° (*c* 1.04); δ_H (D_2O) 5.23 (s, 1H, 1–H), 4.14 (d, 1H, $J_{2,3}$ 2.3 Hz, 2–H), 3.98 (dd, 1H, $J_{3,4}$ 5.7 Hz, 3–H), 4.29 (dd, 1H, $J_{4,5}$ 7.7 Hz, 4–H), 3.88 (m, 1H, $J_{5,6a}$ 3.1, $J_{5,6b}$ 6.5 Hz, 5–H), 3.81 (dd, 1H, $J_{6a,6b}$ 12.2 Hz, 6a–H), 3.67, (dd, 1H, 6b–H); δ_C 108.1 (1–C).

‡ LSIMS (+)-mode (Cs^+, glycerol matrix), *m/z* (I_{rel}, %) for **9**: 525(2) $[Gal_3+K]^+$, 509(3) $[Gal_3+Na]^+$, 487(3.5) $[Gal_3+H]^+$, 325(5) $[Gal_2+H]^+$; for **10**: 687(7.5) $[Gal_4+K]^+$, 671(21) $[Gal_4+Na]^+$, 649(9) $[Gal_4+H]^+$, 525(1) $[Gal_3+K]^+$, 509(2) $[Gal_3+Na]^+$, 487(4) $[Gal_3+H]^+$, 325(18) $[Gal_2+H]^+$, 163(3) $[Gal_1+H]^+$. LSIMS = liquid secondary ion mass-spectrometry.