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Preliminary communication

Cyclic (1 → 6)-β-D-glucopyranose oligomers: synthesis of cyclogentiotriose and cyclogentiotetraose peracetates

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Cyclic (1 → 6)-β-D-glucan oligomers, herein referred to as cyclogentio-oligosaccharides, having *n* glucose residues, have been synthesized by internal cyclisation of linear gentio-oligosaccharides.

In order to prepare cyclic oligomers from bifunctional, linear oligosaccharides, two routes were tested: (*a*) activation of the anomeric position prior to removal of the leaving group (R^4); and (*b*) selective elimination of the leaving group and subsequent activation of the anomeric centre.

Chloride **2** was prepared from compound[1,2] **1** by the action of dichloromethyl methyl ether–boron trifluoride etherate reagent according to Farkas *et al.*[3] Removal of trichloroacetyl ester groups by ammonia in dichloromethane was readily performed in 60 s at 0°.

Cyclisation of **3** in dichloroethane at 60° in the presence of mercuric bromide and molecular sieves led to a mixture of linear and cyclic oligomers. The cyclic trimer was purified by successive deacetylation, gel filtration (Biogel P2), and reacetylation. Crystallisation gave the peracetate **7** in 16% yield from **1**; m.p. 285°, $[\alpha]_D^{22}$ −1.1° (*c* 1, $CHCl_3$).

Anal. Calc. for $C_{36}H_{48}O_{24}$: C, 50.00; H, 5.59. Found: C, 48.78; H, 5.27.

This product was characterized by f.a.b.m.s. (pseudo-molecular ion $(M + Na)^+$ at *m/z* 887) and n.m.r. spectroscopy ($CDCl_3$); ^1H: δ* 4.65 (d, $J_{1,2}$ 7 Hz, H-1), 4.95 (q, $J_{2,3}$ 9.3 Hz, H-2), 5.25 (t, $J_{3,4}$ 9.5 Hz, H-3), 5.03 (t, $J_{4,5}$ 9.5 Hz, H-4), 3.79 (oct, $J_{5,6proR}$ 6.4 Hz, H-5), 3.67 (q, $J_{5,6proS}$ 1.5 Hz, H-6pro*S*), and 4.07 (q, $J_{6proR,6proS}$ 12.3 Hz, H-6pro*R*); ^{13}C: δ† = 100.20 (C-1), 72.20 (C-2), 72.50 (C-3), 68.60 (C-4), 73.55 (C-5), and 68.25 (C-6).

Bromide **6** was prepared by the action of $TiBr_4$ on tetramer **5** by a method previously described[2,4,5]. Autocondensation of **6** in the presence of mercuric cyanide and mercuric bromide under high dilution in toluene–dichloroethane gave a mixture of linear and cyclic oligomers, from which cyclogentiotetraose **8** crystallised in 15% yield from **5**; m.p. 212°, $[\alpha]_D^{20}$ −24° (*c* 1, $CHCl_3$).

*Chemical shifts (δ) for ^1H are expressed in p.p.m. relative to Me_4Si.

†Chemical shifts (δ) for ^{13}C are expressed in p.p.m. relative to the central line of $CDCl_3$ at 77.2 p.p.m.

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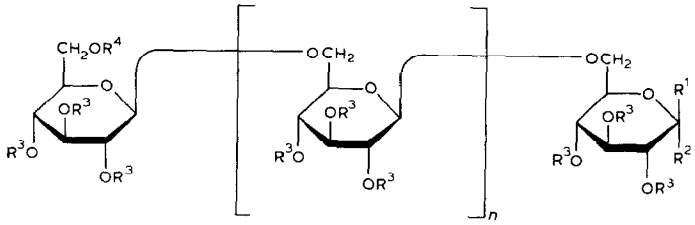
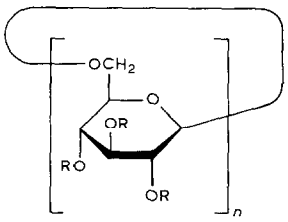


1 $n = 1, R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = CCl_3CO$
2 $n = 1, R^1 = Cl, R^2 = H, R^3 = Ac, R^4 = CCl_3CO$
3 $n = 1, R^1 = Cl, R^2 = H, R^3 = Ac, R^4 = H$
4 $n = 2, R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = CCl_3CO$
5 $n = 2, R^1 = OAc, R^2 = H, R^3 = Ac, R^4 = H$
6 $n = 2, R^1 = H, R^2 = Br, R^3 = Ac, R^4 = H$



7 $n = 3, R = Ac$
8 $n = 4, R = Ac$

Anal. Calc. for $C_{48}H_{64}O_{32}$: C, 50.00; H, 5.59. Found: C, 49.82; H, 5.83.

Characterization of **8** was performed by f.a.b.m.s. (pseudomolecular ion $(M + Na)^+$ at *m/z* 1175) and n.m.r. spectroscopy ($CDCl_3$); ^1H: δ* 4.73 (d, $J_{1,2}$ 7.5 Hz, H-1), 5.02 (q, $J_{2,3}$ 9.5 Hz, H-2), 5.24 (t, $J_{3,4}$ 9.5 Hz, H-3), 5.02 (t, $J_{4,5}$ 9.5 Hz, H-4), and 3.5–4.0 (m, H-5, H-6A, H-6B); ^{13}C: $\delta^\dagger$ 100.55 (C-1), 71.05 (C-2), 73.10 (C-3), 68.75 (C-4), 74.05 (C-5), and 67.5 (C-6).

Computer calculations[6] based on research of minimum-energy conformation of molecules led to a cavity hole of 1 and 3.3 Å for **7** and **8**, respectively; compound **8** should accomodate group IA or IIA cations.

ACKNOWLEDGMENT

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