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Preliminary communication

Formation of cyclo-oligosaccharides by polycondensation of the 3- and 6-*O*-tritylated derivatives of 1,2-*O*-(1-cyanoethylidene)-α-D-galactofuranose

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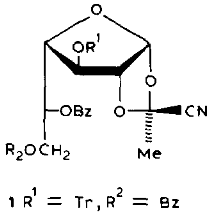
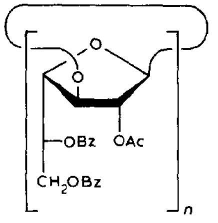
Polycondensation of tritylated 1,2-*O*-(1-cyanoethylidene) derivatives of mono- and oligo-saccharides is a general method for the synthesis of regular homo- and hetero-polysaccharides[1]. It is the fraction of highest molecular weight that is usually subjected to analysis, whereas low-molecular-weight products are not investigated. The d.p. of the polymeric products is determined as a rule from the ratio of terminal, non-reducing glycosyl units to the inner units, or by means of gel-permeation chromatography.

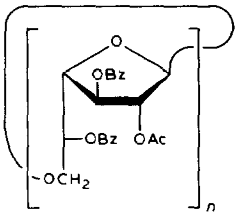
In continuing our studies of the synthesis of regular glycofuranans[2,3], we have carried out the polycondensation of tritylated 1,2-*O*-(1-cyanoethylidene) derivatives[4] **1** and **2** of D-galactofuranose. In each reaction, regular linear polysaccharides were formed[4] together with products which differed sharply from the polysaccharides in chromatographic mobility. Evidence for the cyclic structure of the latter products is now presented.



1 $R^1 = Tr, R^2 = Bz$
2 $R^1 = Bz, R^2 = Tr$



3 $n = 4$
4 $n = 5$



5 $n = 2$
6 $n = 3$
7 $n = 4$

Products of polycondensation of the monomer **1** [high-vacuum technique, CH_2Cl_2 as a solvent, silver trifluoromethanesulfonate (0.1 equiv.) as the initiator, room temperature, 19 h, quenching with aqueous pyridine] were subjected to column chromatography on Silica Gel L (Chemapol, Czechoslovakia, 40/100 μm, chloroform → chloroform–acetone, 9:1) and a fraction containing several compo-

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nents with similar R_F values was obtained in 36% yield. Compounds **3** and **4** were isolated by h.p.l.c. on Ultrasphere C-8 [methanol–water (3:1) → methanol]: **3**, R_F 0.45 [hereinafter Kieselgel 60 (Merck), heptane–ethyl acetate (3:2)], $[\alpha]_D^{25}$ −62° (*c* 1.5, chloroform); **4**, R_F 0.39, $[\alpha]_D^{25}$ −65.5° (*c* 1.4); the polysaccharide had R_F 0.

Likewise, polycondensation of the monomer **2** (42 h) and subsequent column chromatography [benzene → benzene–ethyl acetate (4:1)] afforded **5** {6%, R_F 0.71, $[\alpha]_D^{28}$ −129° (*c* 1.2)}, **6** {5%, R_F 0.59, $[\alpha]_D^{27}$ −79.5° (*c* 2)}, and **7** {10%, R_F 0.53, $[\alpha]_D^{27}$ −41° (*c* 2.7)}; the corresponding polysaccharide had R_F 0–0.2.

The ^{13}C-n.m.r. spectra (Table I) of **3–7** each contained six signals for a repeating galactofuranose residue but none for terminal sugar moieties, indicating these oligosaccharides to be cyclic. The chemical shifts of the ^{13}C signals in **3** and **4** differed from each other (and from those in the spectrum of the polysaccharide, *e.g.*, $\delta_{C\text{-}1}$ 104.90) due to the different sizes of the macrocycles. The same situation holds for the spectra of **5–7**.

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS[a] (δ, P.P.M.) OF **3–7** (BRUKER AM-300, $CDCl_3$, INTERNAL Me_4Si)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
3	107.61	83.42*	81.66*	85.30*	70.54	64.26
4	106.52	81.36*	80.99*	83.64*	70.22	64.13
5	104.95	75.61*	76.09*	82.37	67.75	63.89
6	106.51	80.92*	77.10	81.53*	71.64	66.75
7	106.47	80.92*	77.39	81.60*	70.76	66.42

[a] Assignments marked * may be interchanged. Other signals: δ 20.2–20.8 (CH_3CO), 169.3–169.6 (CH_3CO), 165.4–166.2 (PhCO), 127.8–133.8 (Ph).

The structure of repeating units in **3–7** follows from their ^{1}H-n.m.r. spectra (Table II). The signals (s or bs) for H-1 indicate the 1,2-*trans* configuration. The high-field position of the signal for H-3 in the spectra of **3** and **4** (and for H-6 in the spectra of **5–7**) points to (1→3) and (1→6) linkages.

Deacylation of a mixture of **3** + **4** (0.1M MeONa in chloroform–methanol, then aqueous NaOH) gave the unsubstituted oligosaccharides which were eluted from a column of Fractogel TSK HW-40 in the volumes typical for di- to hexasaccharides. Methylation analysis of these oligosaccharides gave only 1,3,4-tri-*O*-acetyl-2,5,6-tri-*O*-methylgalactitol, identified by its mass spectrum, and in accord with (1→3)-linked galactofuranose residues and a cyclic structure.

The size of the macrocycles in **3–7** was deduced from their f.a.b.-mass spectra: **3**, *m/z* 1650 $[M + 2]^+$; **4**, *m/z* 2063 $[M + 3]^+$; **5**, *m/z* 824 $[M]^+$; **6**, *m/z* 1238 $[M + 2]^+$; **7**, *m/z* 1649 $[M + 1]^+$.

The formation of **3–7** from **1** and **2** is the first example of cyclisation in the polycondensation of tritylated 1,2-*O*-(1-cyanoethylidene) derivatives of sugars. Linear and cyclic oligosaccharides have been isolated after polycondensation of

TABLE II

^{1}H-N.M.R. DATA[a] FOR **3**–**7** (BRUKER WM-250, CDCl$_3$, INTERNAL Me$_4$Si)

Compound	*Chemical shifts (δ) (Coupling constant, Hz)*						
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-5* ($J_{5,6a}$)	*H-6a* ($J_{6a,6b}$)	*H-6b* ($J_{5,6b}$)
3	5.12s*	5.27s*	4.17d	4.61t	5.98m	4.66m	4.90m
	(0)	(0)	(3.0)	(3.0)			
4	5.20s*	5.30s*	4.16dd	4.59dd	5.94m	4.73d	4.73d
	(0)	(0)	(1.7)	(3.0)	(6.0)	(0)	(6.0)
5	5.15bs	5.47dd	5.43dd	4.71dd	5.48m	4.15dd	4.06dd
	(1.3)	(4.5)	(8.8)	(1.7)	(5.5)	(8.8)	(11.0)
6	5.26bs	5.31dd	5.35dd	4.83dd	5.66ddd	4.25dd	3.99dd
	(1.2)	(2.4)	(5.7)	(2.8)	(7.2)	(10.0)	(4.5)
7	5.22bs	5.14dd	5.27dd	4.62dd	5.83m	4.12dd	3.94dd
	(0.9)	(2.0)	(5.2)	(1.5)	(6.0)	(9.0)	(1.0)

[a] Assignments marked * may be interchanged. Acetyl signals are at 1.67, 1.72, 2.10, 1.90, and 1.90 p.p.m. for compounds **3**–**7**, respectively.

hydroxyl-containing acylglycosyl halides under Helferich conditions[5,6]. Cyclisation reactions during polycondensations will lower the yield of the target high-molecular-weight polysaccharides.

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