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Preliminary communication

Stereospecific synthesis of a (1→5)-α-L-arabinan

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Stereospecific polycondensation of tritylated 1,2-*O*-cyanoethylidene derivatives of mono- and oligo-saccharides provides a route for the synthesis of regular homo- and hetero-polysaccharides[1], the synthesis of the O-specific polysaccharide of *Salmonella newington* being an example[2]. The polysaccharides prepared hitherto by this procedure contained exclusively pyranoid units and we now report the synthesis of a polysaccharide containing furanoid units.

The (1→5)-α-L-arabinan (**6**) was prepared *via* polycondensation of 3-*O*-benzoyl-1,2-*O*-[(1-*endo*-cyano)ethylidene]-5-*O*-trityl-β-L-arabinofuranose (**4**). The glycosylation of several trityl ethers of monosaccharides by 1,2-*O*-cyanoalkylidene derivatives of L-arabinofuranose has been shown to be stereospecific[3].

The monomer **4** was prepared as follows. 3,5-Di-*O*-acetyl-1,2-*O*-[(1-*endo*-cyano)-ethylidene]-β-L-arabinofuranose[3] (**1**) was deacetylated (methanolic 0.05M sodium methoxide–pyridine, 1:2; 20°, 30 min) to give 77% of the diol **2***, m.p. 91–92° (from chloroform), $[\alpha]_D^{25}$ +41° (*c* 1.6, acetone), R_F** 0.24 (chloroform–acetone, 3:1). Treat-

TABLE I

^{1}H-N.M.R. DATA[a] FOR **2**–**4**

Compound	*Chemical shift (δ) (Coupling constant, Hz)*						
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4*	*H-5* ($J_{4,5}$)	*H-5'* ($J_{4,5'}$; $J_{5,5'}$)	CH_3
2	6.00d (4.2)	4.80dd (2.9)	4.58dd (7.5)	3.81–3.74m	4.00dd (3.5)	3.87dd (4.5; 12.5)	1.81s
3	5.83d (4.4)	4.71dd (3.0)	4.32dd (6.8)	3.75		3.66m	3.47dd (6.9; 13.7)	1.75s
4	5.96d (4.2)	4.82dd (2.2)	5.33dd (6.9)	4.17dd	3.76dd (6.3)	3.50dd (6.1; 10.0)	1.79s

[a] For solutions in $CDCl_3$ (internal Me_4Si); Bruker WM-250 spectrometer.

*Correct C, H, and N analyses were obtained for **2**–**4**.
**T.l.c. on Kieselgel 60 (Merck).

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ment of **2** with chlorotriphenylmethane (1.3 mol) in pyridine (20°, 18 h) afforded 72% of the 5-trityl ether **3**, m.p. 156–157° (from ether–pentane), $[\alpha]_D^{25}$ +33° (*c* 0.9, chloroform), R_F 0.80 (chloroform–acetone, 3:1). Conventional treatment of **3** with benzoyl chloride (2 mol) in pyridine (20°, 1 h) then gave 86% of **4**, m.p. 76–79° (from toluene–hexane), $[\alpha]_D^{25}$ +18° (*c* 1.1, chloroform), R_F 0.54 (toluene–ethyl acetate, 19:1). The ^{1}H-n.m.r. data for **2**–**4** are given in Table I.

Polycondensation of **4** was performed as described previously[4], *i.e.*, in dichloromethane in the presence of triphenylmethylium perchlorate[2,5] (6 mol%) at 20°. After 15 h, the reaction mixture did not contain tritylated carbohydrate derivatives (t.l.c.). It was treated with aqueous pyridine (to destroy the catalyst), diluted with chloroform, and washed with water. Column chromatography on silica gel (benzene → benzene–ethanol, 9:1) gave 90% of the polysaccharide derivative **5**, $[\alpha]_D^{25}$ −90° (*c* 1.2, chloroform), R_F 0.39–0.60 (benzene–ethanol, 9:1). The ^{13}C-n.m.r. spectrum of **5** (Table II) accorded with the assigned structure (*cf.* the data for acylated methyl 5-*O*-α-L-arabinofuranosyl-α-L-arabinofuranosides[3]). Signals for the cyano group (δ 107–128) and the trityl group (δ ~143 and 85–100) were absent from the spectrum of **5**.

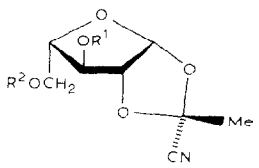
TABLE II

^{13}C-N.M.R. CHEMICAL SHIFTS (δ, p.p.m.) OF **5** AND **6** [a]

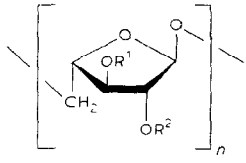
Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*Other signals*
5 [b]	106.15	81.6 [c]	77.5	82.0 [c]	66.2	169.6 (CH_3CO), 165.8 (PhCO), 133.4, 129.95, 129.5, 128.5, 128.4 (Ph), 20.6 (CH_3CO)
6 [d]	108.8	82.1	78.1	83.5	68.2	

[a] Bruker WM-250 spectrometer. [b] Solution in $CDCl_3$ (internal Me_4Si). [c] Assignments may be interchanged. [d] Solution in D_2O (internal MeOH; 50.15 p.p.m. from signal for Me_4Si at 60°.

Deacylation of **5** (methanolic 0.15M sodium methoxide, 20°, 4 h) gave the polysaccharide **6** in almost quantitative yield, $[\alpha]_D^{28}$ −130° (*c* 0.7, water). The $[\alpha]_D$ value of **6** is close to those reported for natural α-L-arabinofuranans[6]. The ^{13}C-n.m.r. spectrum of **6** (Table II) contained only five signals corresponding to the carbon atoms of (1→5)-linked α-L-arabinofuranosyl residues[6b]. This fact indicates the high stereo-



1 $R^1 = R^2 = Ac$
2 $R^1 = R^2 = H$
3 $R^1 = H, R^2 = Tr$
4 $R^1 = Bz, R^2 = Tr$



5 $R^1 = Bz, R^2 = Ac$
6 $R^1 = R^2 = H$

and regio-specificity associated with the polycondensation of **4**, and is in keeping with the results of model glycosylations[3].

The absence from the ^{13}C-n.m.r. spectra of **5** and **6** of signals for terminal non-reducing arabinofuranosyl groups indicates a high d.p. The major portion of **6** was eluted from a column of Bio-Gel P-4 in the void volume, indicating a molecular weight of 2,000–3,000 (d.p. 15–23).

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