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Preliminary communication

Stepwise synthesis of linear β-D-(1→3)-xylo-oligosaccharides. Preparation of a β,β,β-D-linked tetrasaccharide derivative

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A characteristic feature of D-xylans as constituents of the cell wall of marine algae is the presence of (1→3) and (1→4) linkages between the D-xylose units of the polysaccharide skeleton[1]. It is also well known that the cell walls of several green algae are constituted principally of a D-xylan in which the D-xylose residues are linked[2–7] exclusively β-(1→3). In this respect, the structure of a D-xylan isolated from *Rhodymenia palmata* was determined chemically (methylation–hydrolysis analysis), by Percival and Chanda[8], and Barry *et al.*[9], to consist essentially of a linear chain of about 40 D-xylose units, with random (1→3)- and (1→4)-linkages according to the enzymic studies of Björndal *et al.*[10]. On the other hand, the D-xylan of the cell wall of the green seaweed *Penicillus dumetosus* was determined, by chemical investigation[6], to consist of a linear chain of β-(1→3)-linked D-xylose units, in accord with our recent ^{13}C-n.m.r. study of this polysaccharide.

Extending our work in the D-xylose series by the preparation of synthetic model compounds for n.m.r. investigations on D-xylans[11], we synthesized stepwise β,β,β-(1→3)-linked, linear D-xylo-oligosaccharides up to an acetylated tetramer having a temporary trichloroacetyl group at O-3 of the terminal, nonreducing group (**7**) in view of preparing higher-mol.-wt. oligomers. We are reporting herein the ^{1}H-n.m.r. (Fig. 1, Table I) and ^{13}C-n.m.r. data (Table II) of **7**.

O-(2,4-di-*O*-Acetyl-3-*O*-trichloroacetyl-β-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-*O*-(2,4-di-*O*-acetyl-β-D-xylopyranosyl)-(1→3)-1,2,4-tri-*O*-acetyl-β-D-xylopyranose was prepared, by stepwise synthesis, by addition of 2,4-di-*O*-acetyl-3-*O*-trichloroacetyl-α-D-xylopyranosyl bromide (**1**) to **2** having OH-3 free[12] in 1,2-dichloroethane and in the presence of mercury salts [$Hg(CN)_2$, $HgBr_2$]. The homogeneous, β-D-linked compound **3** (m.p. 143°; $[\alpha]_D^{20}$ −60°) was isolated by silica gel column chromatography, the trichloroacetyl group removed by stirring with methanol–pyridine–1,2-dichloroethane (reaction monitored by t.l.c.), and the resulting, OH-3 free disaccharide **4** (m.p. 142.5°, $[\alpha]_D^{20}$ −57°) submitted to further addition of **1**. The stepwise synthesis led

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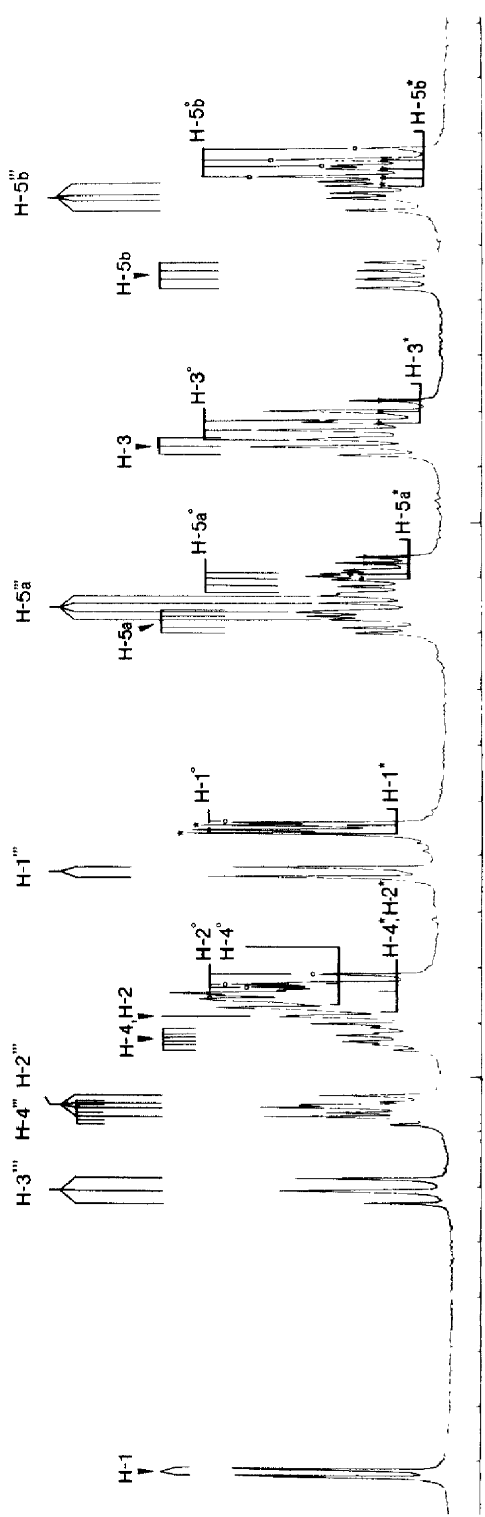


Fig. 1. ^{1}H-n.m.r. spectrum of **7** recorded at 400 MHz with a Bruker WH spectrometer equipped with an Aspect 2000 computer for a solution in $CDCl_3$ and Me_4Si as internal standard. Most assignments were determined at 250 MHz with a Cameca spectrometer by homodecoupling or INDOR (internuclear double resonance) experiments and completed at 400 MHz by pseudo-INDOR or spin-tickling experiments. Chemical shifts and coupling constants were determined unambiguously both for the reducing and nonreducing residues. Distinction between the two sets of data for the two units in the middle of the chain was not achieved and H signals were labelled H° and H* for each unit.

TABLE I

^{1}H-N.M.R. DATA FOR COMPOUND 7[a]

Unit	*H-1*	*H-2*	*H-3*	*H-4*	*H-5a*	*H-5b*
Reducing (H)	5.72	4.89	3.86	4.93	4.18	3.55
	(5.28)	(6.52)	(6.39)	(4.10, 6.17)[b]	(12.47)	
Middle (H°)	4.54	4.82	3.83	4.85	4.11	3.35
	(5.82)	(6.95)	(6.87)	(4.69, 7.46)[b]	(12.03)	
Middle (H*)	4.55	4.86	3.80	4.86	4.08	3.37
	(6.13)	(7.59)	(7.57)	(4.34, 6.87)[b]	(12.23)	
Nonreducing terminal (H''')	4.63	5.05	5.20	5.06	4.15	3.41
	(6.90)	(9.07)	(8.75)	(5.42, 8.64)[b]	(11.89)	

[a] For solutions in chloroform. δ Values relative to the signal of Me_4Si as internal reference. Coupling constants in parentheses in Hz. δ and J values were confirmed by iterative fitting of the experimental spectrum with the ITRCAL program. [b] The lower value corresponds to $J_{4,5a}$ and the higher to $J_{4,5b}$.

TABLE II

^{13}C-N.M.R. DATA FOR COMPOUND 7[a]

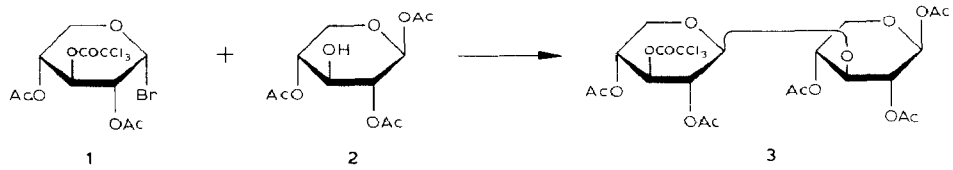
Carbon atom	*Unit*			
	Middle and nonreducing			*Reducing*
1	101.00	100.47	99.94	91.88
3	76.17	75.95	75.81	75.52
2 and 4	71.29	70.61	69.89	69.62
	69.35	69.13	68.55	68.55
5	62.09	61.92	61.78	61.37

[a] The spectrum was recorded at 62.86 MHz with a Cameca spectrometer for a solution in chloroform with Me_4Si as internal standard. Assignments were partially determined in four sets as C-1, -3, -2 and -4, and -5.

to 7 *via* 5 (m.p. 190°; $[\alpha]_D^{20}$ −52°) and 6 (m.p. 213°, $[\alpha]_D^{20}$ −70°)*. Compound 7 crystallized from chloroform–ethyl ether, m.p. 160°, $[\alpha]_D^{20}$ −76.8° (*c* 1, $CHCl_3$).

Anal. Calc. for $C_{40}H_{51}Cl_3O_{27}$ (1070.2): C, 44.89; H, 4.80; Cl, 9.94. Found: C, 44.39; H, 4.86; Cl, 9.52.

*Satisfactory elemental analyses and n.m.r. data were obtained for these compounds; values of $[\alpha]_D^{20}$ are given for a solution in $CHCl_3$ (*c* 1).



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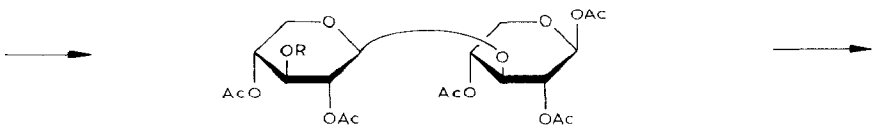
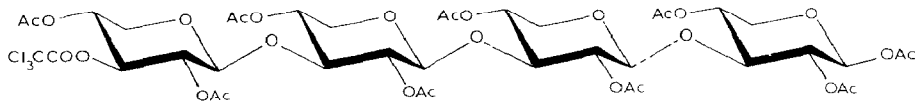


4 R = H

5 R = 2,4-di-*O*-acetyl-3-*O*-trichloroacetyl-β-D-xylopyranosyl

6 R = 2,4-di-*O*-acetyl-β-D-xylopyranosyl



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