

Preliminary communication

Synthesis of β -D-(1 \rightarrow 2)-linked D-glucopentaose, a part of the structure of the exocellular β -D-glucan of *Agrobacterium tumefaciens**

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The exocellular D-glucan formed by the crown-gall microbe *Agrobacterium tumefaciens* was reported to consist principally of β -D-(1 \rightarrow 2)-linked D-glucopyranosyl residues². Recently, ¹³C-n.m.r. data for the glucopentaose obtained by acid degradation of the polysaccharide were reported by Gorin *et al.*³. We describe here an unambiguous synthesis of β -D-(1 \rightarrow 2)-glucopentaose (1), the ¹³C-n.m.r. spectrum of which (see Fig. 1)

β -Glc-(1 \rightarrow 2)- β -Glc-(1 \rightarrow 2)- β -Glc-(1 \rightarrow 2)- β -Glc-(1 \rightarrow 2)- β -Glc

1

was found to be identical with that reported³, thus providing solid support for the proposed (1 \rightarrow 2)- β -D-glucan structure.

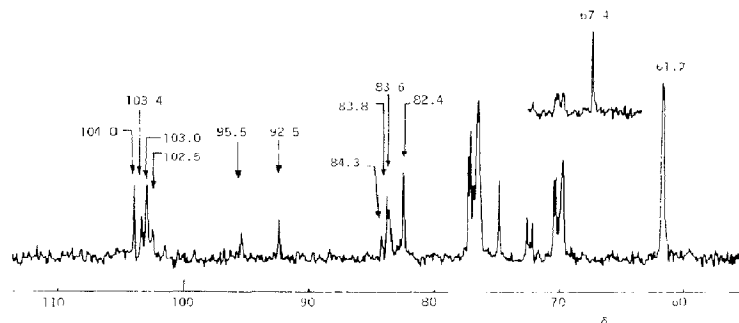
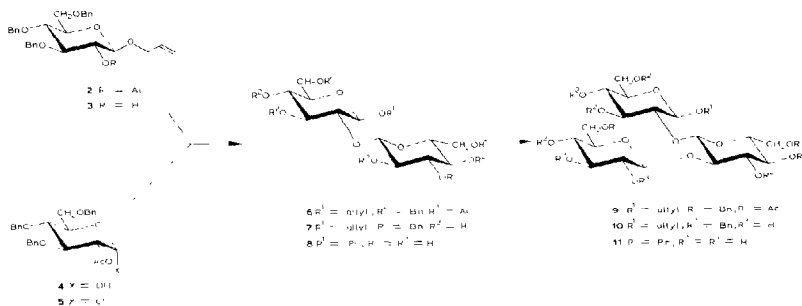


Fig. 1. ¹³C-N.m.r. spectrum of pentasaccharide 1 in D₂O at 70°. [The values of δ_C are expressed in p.p.m. downfield from tetramethylsilane, referenced indirectly with an internal standard of 1,4-dioxane (δ_C 67.40).]

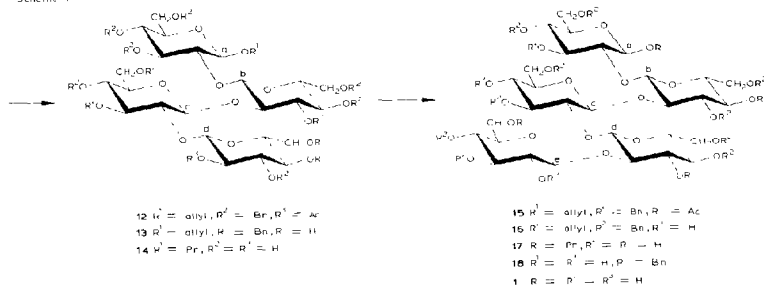
*Glucan Synthesis, Part IV. For Part III, see ref. 1.

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The synthesis of **1** was achieved by a linear, stepwise strategy, using **3** as the starting glycosyl acceptor and **5** as the β -D-glucopyranosyl donor. Deallylation of **2** with $\text{PdCl}_2\text{--AcONa--aq. AcOH}^4$ gave a 70% yield of **4**, $[\alpha]_D +54.6^{\circ}$ ***, m.p. 128.5–129.0° (*i*Pr₂O), which was subsequently treated with $\text{SOCl}_2\text{--DMF}^5$ in CH_2Cl_2 , to give a quantitative yield of **5**, δ_{H} (CDCl_3): 6.30 (H-1, d, J 3.95 Hz). Glycosylation of **3** with **5** in the presence of $\text{AgOSO}_2\text{CF}_3$ and powdered molecular sieves **4A** in $\text{Cl}(\text{CH}_2)_2\text{Cl}$ afforded a 95% yield of **6**, $[\alpha]_D -3.9^{\circ}$, δ_{C} (CDCl_3): 101.4 (C-1a, $^1J_{\text{CH}}$ 161.1 Hz) and 100.3 (C-1b, $^1J_{\text{CH}}$ 163.6 Hz). Deacetylation of **6** in NaOMe--MeOH to give **7** and glycosylation of **7** with **5**, under the conditions just described, proceeded to give a 98% yield of **9**, $[\alpha]_D -0.56^{\circ}$, δ_{C} (CDCl_3): 101.0, 100.6, and 100.1 for C-1_{a,b,c}, with $^1J_{\text{CH}}$ 161 Hz. Deacetylation of **9** to give **10**, $[\alpha]_D +4.27^{\circ}$, and subsequent glycosylation of **10** with **5** afforded a 75% yield of the protected D-glucotetraoside **12**, $[\alpha]_D -0.63^{\circ}$, δ_{C} (CHCl_3): 101.6, 101.3, 100.4, and 100.1 for C-1_{a,b,c,d} with $^1J_{\text{CH}}$ 163 Hz. Deacetylation of **12** to give **13**, followed by glycosylation with **5**, gave an 83% yield of **15**, $[\alpha]_D -3.18^{\circ}$, δ_{C} (CDCl_3): 101.6, 101.2, 100.9, 100.5, and 100.1 for C-1_{a,b,c,d,e}. Deacetylation of **15**, to give a 78% yield of **16**, $[\alpha]_D +9.52^{\circ}$, and deallylation⁴ of **16**, afforded a 67% yield of **18** as a mixture of the α and β anomer in the ratio of 1:1.



Scheme 1



Scheme 2

***Values of $[\alpha]_D$ were measured for CHCl_3 solutions at 25°, unless noted otherwise. Compounds with $[\alpha]_D$ recorded gave satisfactory data for elemental analyses.

Finally, debenzoylation **18** by catalytic hydrogen transfer⁶ in the presence of 10% Pd/C in 10:1 MeOH-HCOOH, afforded the target D-glucopentaose **1**. The β -D configurations of the four anomeric carbon atoms introduced by the glycosylations were assigned by the ¹³C-n.m.r. data for the intermediates **6**, **9**, **12**, and **15**, and were further confirmed by the ¹H-n.m.r. data (see Table I) for the propyl glycosides **11**, **14**, and **17**, which were prepared by debenzoylation⁶ of **10**, **13**, and **16**, respectively.

TABLE I

400-MHz, ¹H-N.M.R. DATA (D₂O, ΔT 60°) FOR β -Glc-(1 \rightarrow 2)- $\{\beta$ -Glc(1 \rightarrow 2) $\}_n$ - β -Glc-1-OPr^a

n	H-1				
	a	b	c	d	e
1	4.546(7.81)	4.805(7.81)	4.814(7.81)		
2	4.548(7.82)	4.827(8.06)	4.827(8.06)	4.884(7.81)	
3	4.544(7.94)	4.814(8.54)	4.834(7.94)	4.882(7.63)	4.886(7.63)

^a The values of δ_H are expressed in p.p.m. downward from the internal standard, sodium 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate. The values in parentheses are ²J_{HH} values expressed in Hz.

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REFERENCES

1. T. Ogawa and T. Kaburagi, *Carbohydr. Res.*, **110** (1982) C12-C15.
2. E. W. Putman, A. L. Potter, R. Hodgson, and W. Z. Hassid, *J. Am. Chem. Soc.*, **72** (1950) 5024-5026; P. A. J. Gorin, J. F. T. Spencer, and D. W. S. Westlake, *Can. J. Chem.*, **39** (1961) 1067-1073.
3. E. Barreto-Bergter, C. R. Camargo, L. R. Hogge, and P. A. J. Gorin, *Carbohydr. Res.*, **82** (1980) 366-371.
4. T. Ogawa and S. Nakabayashi, *Carbohydr. Res.*, **93** (1981) C1-C5; T. Ogawa, S. Nakabayashi, and T. Kitajima, *ibid.*, **114** (1983) 225-236.
5. M. S. Newman and P. K. Sujeebh, *J. Org. Chem.*, **43** (1978) 4367-4369; see also, ref. 4.
6. B. El Amin, G. M. Anantharamaiah, G. P. Royer, and G. E. Means, *J. Org. Chem.*, **44** (1979) 3442-3444; V. S. Rao and A. S. Perlin, *Carbohydr. Res.*, **83** (1980) 175-177.