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Preliminary communication

Synthesis of a branched D-glucoheptaose: the repeating unit of extracellular α-D-glucan 1355-S of *Leuconostoc mesenteroides* NRRL B-1355*

TOMOYA OGAWA** and TOSHIAKI KABURAGI
The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 (Japan)

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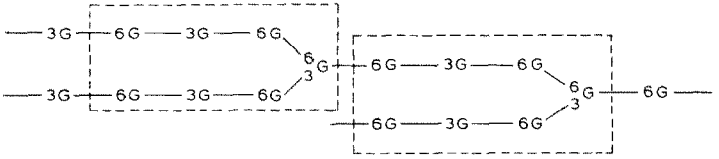
In 1980, Misaki *et al.*[2] proposed for α-D-glucan 1355-S of *Leuconostoc mesenteroides* B-1355 the ramified structure **1**, which involves an alternating arrangement of (1 → 6)- and (1 → 3)-α-D-glucopyranosyl linkages.



1 (G = α-D-glucopyranosyl residue)

As part of a project on the synthesis of branched D-glucans of biological interest, we describe here a stereoselective synthesis of D-glucoheptaose **2**, the repeating unit of **1**. The key intermediates for the convergent synthesis of **2** were designed to be the partially protected D-glucotriose **3** as the D-glucosyl acceptor, and the specifically protected, D-glucobiosyl chloride **4** as the α-D-glucosyl donor.

Synthesis of **4** was achieved as follows, starting from allyl α-D-glucopyranoside[3]; benzylidenation thereof with[4] benzaldehyde and $ZnCl_2$ afforded an 80% yield of the 4,6-benzylidene acetal **5**, $[\alpha]_D$*** +112.3°. Monobenzylation of **5** by the stannylidene method[5] gave a 74% yield of the 2-benzyl ether **6**, m.p. 75–76°, $[\alpha]_D$ +145.1°, along with a 9.2% yield of the 3-benzyl ether, m.p. 143.5–144.5°, $[\alpha]_D$ +95.1°. Reductive cleavage of the benzylidene group of **6** with[6] $LiAlH_4$–$AlCl_3$ gave a 71% yield of the dibenzyl ether **7**, m.p. 57–58°, $[\alpha]_D$ +126.1°. Selective monoacetylation of **7** with AcCl–pyridine–CH_2Cl_2 afforded an 80% yield of acetate **8**, $[\alpha]_D$ +107.1°. D-Glucosylation of **8** with **9** in the pre-

*Glucan Synthesis, Part III. For Part II, see ref. 1.
**To whom enquiries should be addressed.
***Values of $[\alpha]_D$ were measured for $CDCl_3$ solutions at 25°, unless noted otherwise. Compounds having $[\alpha]_D$ recorded gave satisfactory data for elemental analyses.

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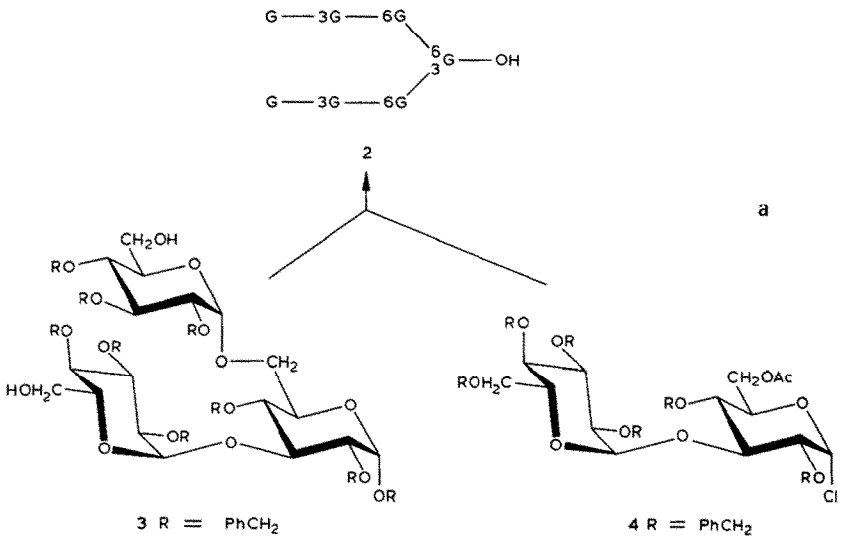
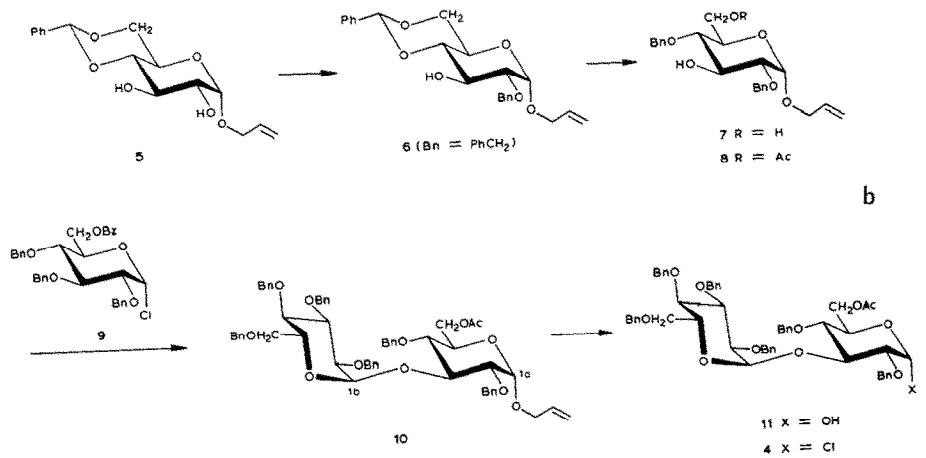
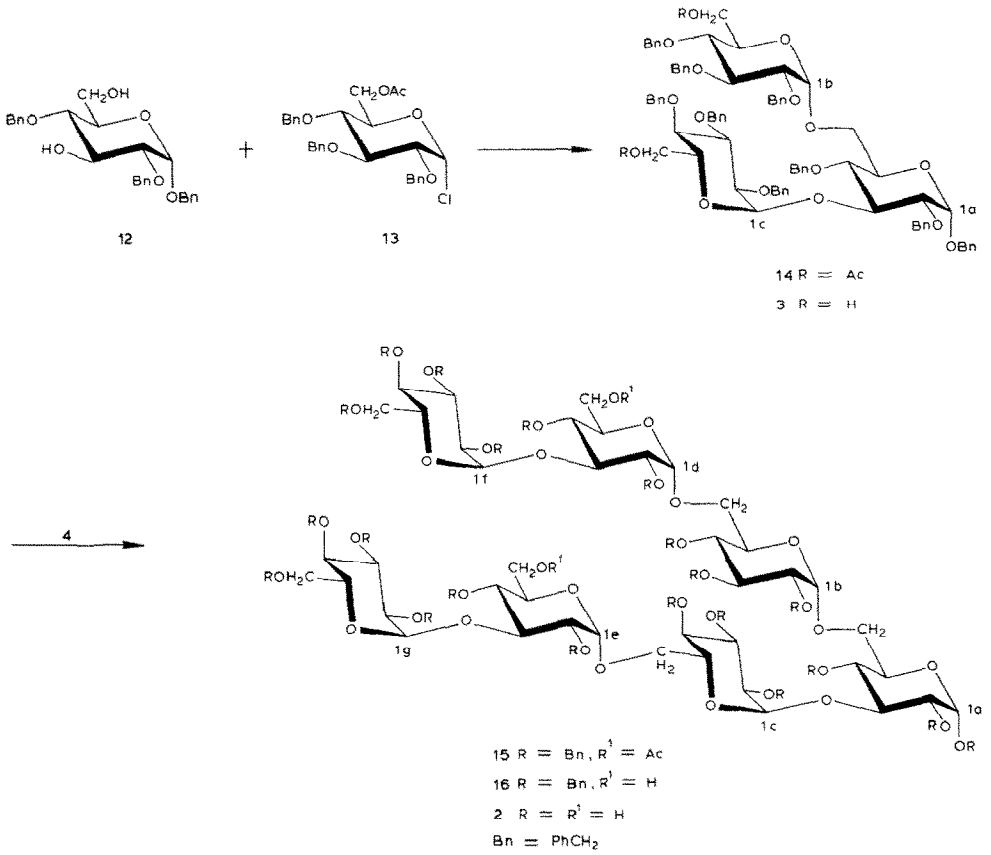


sence of[7] $AgOSO_2CF_3$–$Me_2NCONMe_2$ afforded a 78% yield of a mixture of **10** {$[\alpha]_D$ +71.5°; δ_C ($CDCl_3$): 97.44 ($^1J_{CH}$ 169.9 Hz, C-1b) and 95.06 ($^1J_{CH}$ 167.0 Hz, C-1a)} and its β anomer {$[\alpha]_D$ +42.2°; δ_C ($CDCl_3$): 102.51 ($^1J_{CH}$ 164.6 Hz, C-1b) and 95.10 ($^1J_{CH}$ 168.9 Hz, C-1a)}, in the ratio of 5:2. Deallylation of **10** in the presence of $PdCl_2$ in MeOH gave hemiacetal **11**, which was transformed into chloride **4** in 88% yield by treatment[8] with $SOCl_2$–$HCONMe_2$.



For the synthesis of the D-glycosyl acceptor **3**, a highly stereoselective introduction[1] of two α-D-glucopyranosyl groups, at O-3 and O-6, of **12** is required. In this respect, use of the D-glucopyranosyl chloride[9] **13** carrying a 6-O-acetyl group was expected to be efficient[10]. Thus, D-glucosylation of **12** with **13** in the presence of $AgOSO_2CF_3$ and molecular sieves 4A gave **14** {$[\alpha]_D$ +82.2°; δ_C ($CDCl_3$): 97.34 ($^1J_{CH}$ 170.9 Hz, C-1b, C-1c) and 94.33 ($^1J_{CH}$ 166.0 Hz, C-1a)}; and deacetylation of **14** with MeOH–MeONa afforded a 41% yield of **3**, $[\alpha]_D$ +87.7°; R_F 0.39 in 2:1 toluene–EtOAc.

Finally, the highly stereoselective glycosylation of **3** with **4** (containing a 6-O-acetyl group) was performed at –20° in the presence of $AgOSO_2CF_3$ and molecular sieves 4A in CH_2Cl_2, to give the completely protected D-glucoheptaose **15**, which was deacetylated to give a 36% yield of **16**, $[\alpha]_D$ +93.0°, R_F 0.43 in 3:1 toluene–EtOAc. Catalytic hydrogenolysis of **16** in the presence of 10% Pd–C in MeOH–THF afforded the desired D-glucoheptaose **2**, $[\alpha]_D$ +196.0° (*c* 0.25, H_2O); R_F 0.21 in 3:3:2 iPrOH–EtOH–H_2O; δ_H (D_2O): 5.334 (bs, 3 H, H-1c,1f,1g), 4.976 (bs, 3 H. H-1b,1d,1e), 5.266 (d, *J* 4 Hz, H-1aα), and 4.683 (d, *J* 8.4 Hz, H-1aβ); δ_C (D_2O): 99.50 ($^1J_{CH}$ 171.9 Hz, C-1c,1f,1g), 98.25 ($^1J_{CH}$ 170.9 Hz, C-1b,1d,1e), 96.43 (C-1aβ), and 92.57 (C-1aα). The ^{13}C-n.m.r. data



for synthetic **2** were in good agreement with those of the natural D-glucan reported by Seymour and Knapp[11], thus supporting the proposed structure **1**.

In conclusion, the target molecule, namely, D-glucoheptaose (**2**), was synthesized in a stereocontrolled way by employing the D-glucobiosyl chloride **4** and the D-glucotrioside **3** as the key intermediates.

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REFERENCES

1 T. Ogawa and T. Kaburagi, *Carbohydr. Res.*, 103 (1982) 53–64.
2 A. Misaki, M. Torii, T. Sawai, and I. J. Goldstein, *Carbohydr. Res.*, 84 (1980) 273–285.
3 E. A. Talley, *J. Am. Chem. Soc.*, 67 (1945) 2037–2039.
4 J. W. VanCleve, *Carbohydr. Res.*, 17 (1971) 461–464; D. M. Hall, *ibid.*, 86 (1980) 158–160.
5 C. Augé, S. David, and A. Veyrières, *J. Chem. Soc., Chem. Commun.*, (1976) 375–376; R. M. Munavu and H. H. Szmant, *J. Org. Chem.*, 41 (1976) 1832–1836; M. A. Nashed and L. Anderson, *Tetrahedron Lett.*, (1976) 3503–3506; *Carbohydr. Res.*, 56 (1977) 325–336.
6 A. Lipták, I. Jodál, and P. Nánási, *Carbohydr. Res.*, 44 (1975) 1–11.
7 S. Hanessian and J. Banoub, *ACS Symp. Ser.*, 39 (1976) 36–64; *Carbohydr. Res.*, 53 (1977) C13–C16.
8 F. Sugawara, H. Nakayama, and T. Ogawa, *Carbohydr. Res.*, 108 (1982) C5–C9; see also M. S. Newman and P. K. Sujeeth, *J. Org. Chem.*, 43 (1978) 4367–4369.
9 G. Zemplén, Z. Csürös, and S. J. Angyal, *Ber.*, 70 (1937) 1848–1856; N. Pravdić and D. Keglević, *Tetrahedron*, 21 (1965) 1897–1901.
10 T. Ishikawa and H. G. Fletcher, Jr., *J. Org. Chem.*, 34 (1969) 563–571; P. J. Pfäffli, S. H. Hixon, and L. Anderson, *Carbohydr. Res.*, 23 (1972) 195–206; J. M. Fréchet and C. Schuerch, *J. Am. Chem. Soc.*, 94 (1972) 604–609; S. Koto, T. Uchida, and S. Zen, *Bull. Chem. Soc. Jpn.*, 46 (1973) 2520–2523.
11 F. R. Seymour and R. D. Knapp, *Carbohydr. Res.*, 81 (1980) 67–103.