

## Synthesis of 1,2,3,4-Tetra-O-(4-Methoxyphenylmethyl)- $\alpha$ -D-Glucopyranoside As a Building Block

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(Received June 1, 1997)

### abstract

Synthetic routes are described a new protecting glucopyranoside, 1,2,3,4-tetra-O-(4-methoxyphenylmethyl)- $\alpha$ -D-glucopyranoside. This compound was synthesized via six steps and may be interesting as a building block for the synthesis of Oligosaccharides.

### Introduction

In recent years the glycons of glycoconjugates and antibiotics in molecular recognition for the transmission of biological information about membranes, cell walls, and antibiotics have made remarkable biological progress<sup>1)</sup>. For these biological aspects, these naturally occurring products are attractive by organic synthetic chemist.

Oligosaccharide (1) isolated by digestion of suspension-cultured sycamore cell walls has an anti-auxin activity and was synthesized by Ogawa<sup>2)</sup>. Oligosaccharide (2) isolated from soybean is an elicitor activating the biosynthesis of phytoalexin and was synthesized by Lorentzen<sup>3)</sup> (Fig.1).

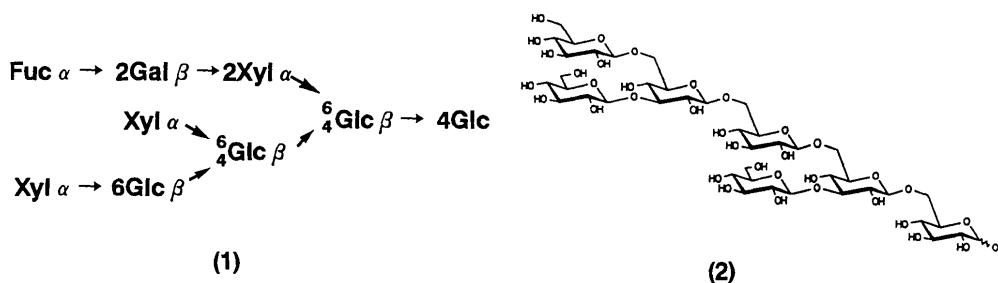


Fig.1

Glucose-containing Oligosaccharide (1) and (2) were synthesized by 1,2-cis- $\alpha$ -gluco type glycosylations in which 1,2,3,4-Tetra-O-Benzyl- $\alpha$ -D-Glucopyranoside (3) was used as a glycosyl acceptor.

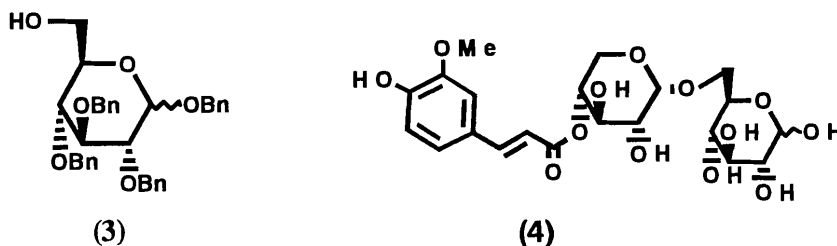


Fig.2

Interesting in the biological aspects<sup>4)</sup> we planed to synthesis of feruloyl xyloglucan (4) isolated from cell walls of growing bamboo shoots<sup>5)</sup>. But we were not able to use glucopyranosideo (3) as a glycosyl acceptor because feruloyl group underwent hydrogenation when removed benzyl protection groups. By this reason we required the new suitable building for the synthesis of oligosaccharides.

We now report new protecting glucose, 1,2,3,4-tetra-*o*-(4-methoxybenzyl) -  $\alpha$ -D-glucopyranoside (5). 4-Methoxybenzyl (MPM) group was prepared in mild condition (MPMCl/NaH or MPM trichloroacetimidate/cat.trifluoromethanesulfonic acid<sup>6)</sup>) and was easily removed by cerium(IV) ammonium nitrate (CAN)<sup>7)</sup>.

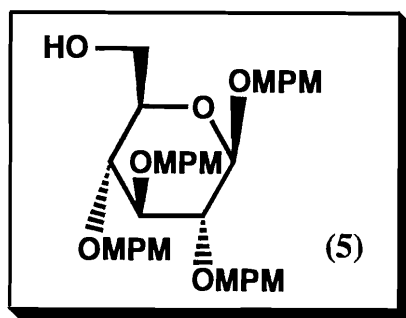
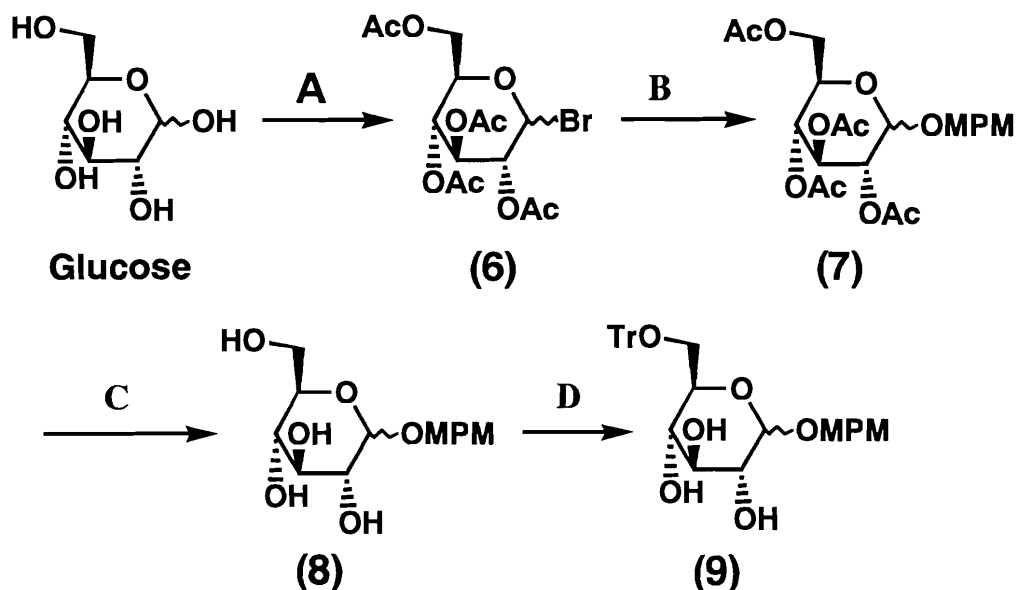


Fig.3

## Result and Discussion

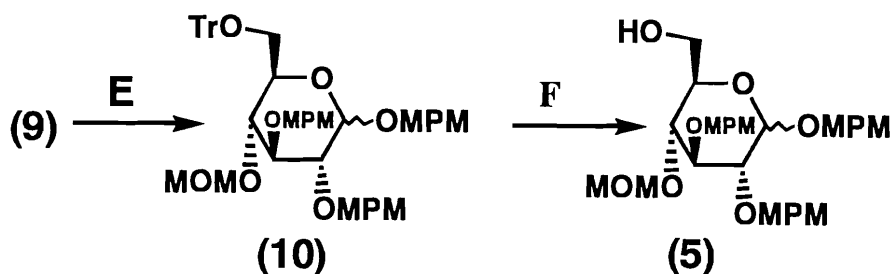
Glucose was treated following the same procedure reported by Barczai-Martos<sup>8)</sup> to give bromoacetate (6). 1-Protected glucopyranoside (7) was obtained by treatment of (6) with MPM-OH (4-methoxybenzyl alcohol) in the presence of HgO, HgBr<sub>2</sub> and drierite<sup>9)</sup> in 67%. Hydrolysis of (7) with methanolic-NaOMe easily afforded tetra-ol (8) in 90% yield. Selective protection of 1-hydroxy group was accomplished by TrCl (trityl chloride), DMAP, and Et<sub>3</sub>N in DMF in 68% yield.



A) Mrthod<sup>9)</sup>. B) MPMOH, HgO, HgBr<sub>2</sub>, drierite, CH<sub>2</sub>Cl<sub>2</sub>, 67%. C) methanolic NaOMe, MeOH, 90%. D) TrCl, DMAP, Et<sub>3</sub>N, DMF, 68%.

Scheme 1

Remaining hydroxy group of tritylate (9) was protected with MPM-Cl and NaH in 77%. Selective deprotection was achieved by formic acid to afford target compound (5)<sup>10)</sup> in 85%.



E) NaH, THf then MPMCl, 77%. F) HCOOH, ether, 85%

Scheme 2

Title compound (5) was easily synthesized in six steps from glucose. Recently, the glycons for their biological aspects<sup>11)</sup> are attractive by organic synthetic chemist. Considering these facts, title compound (5) will be a useful building block for the synthesis of a Oligosaccharide.

### Acknowledgments

We thank Mr. T. Takamatsu, Mr. T. Izumori and Mr. J. Sato, Faculty of Science, Hirosaki university, for measurement of 270-MHz NMR.

### References

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- 10) Compound (5) : IR : 1615, 1514, 1464  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.35-7.15 (m, 8H), 6.92-6.89 (m, 8H), 4.90-4.48 (m, 10H), 3.80 (s, 3H), 3.79 (s, 6H), 3.78 (s, 3H), 3.75-3.25 (m, 6H)
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