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# Synthesis of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside from *α*-D-glucose

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*Abstract*: Some of simple carbohydrates and their derivatives are used for the clinical treatment of various diseases. Epoxide derivatives, which can be obtained by the intramolecular elimination of water from two vicinal hydroxyl groups, are stable, but sufficiently reactive compounds very often used as intermediaries in various syntheses. Synthesis of epoxide derivative, methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside from *α*-D-glucose was achieved in high yields in the minimal number of synthetic steps. Anhydrous glucose was used as a starting material which was transformed into methyl *α*-D-glucopyranoside using dry, gaseous hydrogen chloride. Thus obtained derivative was treated with benzaldehyde in the presence of zinc chloride as Lewis acid giving methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside. The obtained compound was treated with *N*-bromosuccinimide (NBS) in dichloromethane in the presence of barium carbonate giving methyl 4-*O*-benzoyl-6-bromo-6-deoxy-*α*-D-glucopyranoside. In the next step, the obtained compound was treated with *tert*-butyldimethylsilyl chloride (TBDMSCl) in pyridine, and methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside was further mesylated, and the obtained methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-*α*-D-glucopyranoside was treated at the end with KOH to give methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside (yield 78 %).

*Keywords*: D-allose derivative; 3,4-epoxide ring; selective silylation; carbohydrates.

## INTRODUCTION

When there are two present OH groups in 1,2- or 1,3-positions in a molecule, their protection can very often be achieved by forming acetals, ketals and

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ortho esters. This is particularly significant in the synthesis of carbohydrates.[1,2] Some of simple carbohydrates and their derivatives are used for the clinical treatment of various diseases.[3] The most often used procedure for their formation is the treatment of glycol with the excess of aldehyde or ketone in the presence of an acidic catalyst.[4] As acid catalysts gaseous hydrogen chloride can be used, sulphuric and *p*-toluenesulphonic acid (from protic acids), and the most frequently zinc chloride as Lewis acid. Another way is to put anhydrous copper salt which binds water.[5] The third way is to introduce acetals and ketals into the reaction mixture instead of aldehydes themselves and then perform the acid catalysed exchange of acetal groups.[4] It is rarely possible to obtain acetals or ketals from vicinal dihalogenides and glycols under the $S_N2$ mechanism.[6]

Benzylidene acetals are mostly used in the carbohydrate chemistry[1,2] and they can be obtained by the treatment of carbohydrates and benzaldehydes with the acid catalysts, such as hydrogen chloride, sulphuric acid, *p*-toluenesulphonic acid and zinc chloride. Besides, it can be used dimethyl or diethyl-acetals of benzaldehyde in the acid media. The main advantage of this group is that it can be removed by catalytic hydrogenation, and the main disadvantage is that both possible diastereoisomers can be obtained during benzylidation.

The most often used agent for the selective protection of hydroxyl groups is *tert*-butyldimethylsilyl chloride (TBDMSCl). *tert*-Butyldimethylsilyl group[7] is appropriate for the temporary protection of hydroxyl groups because it is stable in the wide region of the reaction conditions, and it can be easily removed by the treatment with acids or fluoride ion, and tailor-made ionic liquids ([dihexaEGim][OMs]/*tert*-amyl alcohol media system).[8] This group is recommended for the selective protection of nucleosides,[9] hexopyranosides[10] and other carbohydrate derivatives.[9]

Epoxides or oxiranes can be obtained by the intramolecular elimination of water from two vicinal hydroxyl groups. They are stable, but sufficiently reactive compounds, very often used as intermediaries in various syntheses.[11] The most frequent way of their synthesis is the treatment of an $\alpha$-hydroxy-sulfonic ester with bases. The first step of the reaction is the formation of alkoxide ion, either by deprotonation of hydroxyl group, or by the hydrolysis of carbonic ester using any base. In the second step, it comes the attack of alkoxide ion on the C-atom to which $-OSO_2R$ group is attached, which is followed by the closure of the epoxide ring, with the inversion of configuration at the electrophilic C-atom. Leaving groups can also be the esters of sulphuric or nitric acids, halides, protonated amino groups, diazonium ions, *etc.*, beside the sulphonic ester.

Two epoxide derivatives in two different decades were synthesized at the Laboratory for Organic Synthesis, Faculty of Sciences and Mathematics, University of Niš, and the synthesis of one of them was published at the end of 1980s.[12] Therefore, the novelty in this research is the synthesis of the second

epoxide derivative methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6--deoxy-*α*-D-allopyranoside (Fig. 1) from *α*-D-glucose, where it was obtained in similar yields to the previously published epoxide derivative[12]. It can be an intermediary in the synthesis of biologically active compounds. To the best of our knowledge, two new compounds not previously reported were synthesised in this work: methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-3-*O*--mesyl-*α*-D-glucopyranoside and methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside.

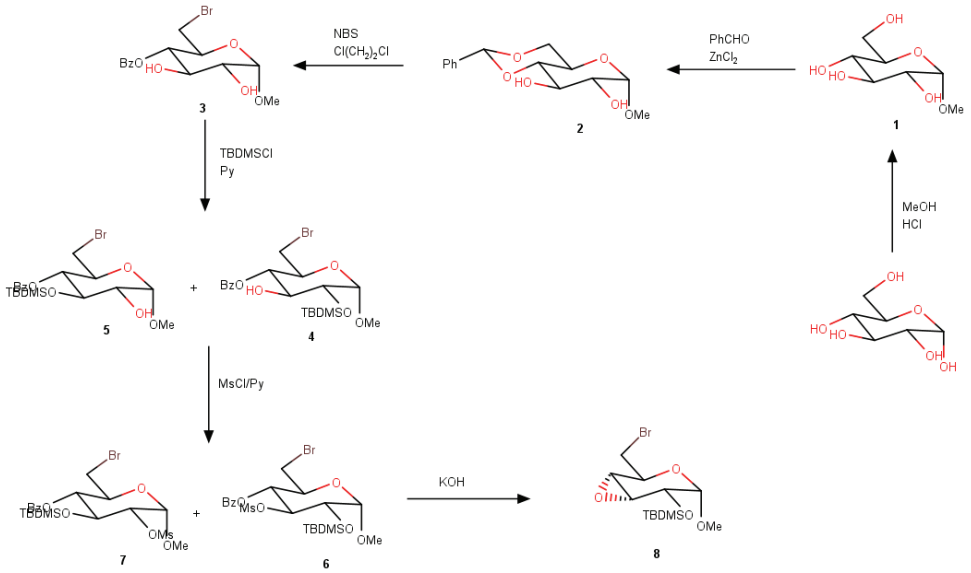


Fig. 1. Synthesis of methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D--allopyranoside (**8**) from *α*-D-glucose.

## EXPERIMENTAL

### *Apparatus*

The NMR analyses were performed on a Bruker AC-250 instrument with the standard Bruker software. All analyses were carried out using regular 5 mm NMR tubes.

### *Reagents*

All chemicals used for syntheses were of the analytical reagent grade. The solutions were prepared for NMR analyses in $CDCl_3$ (Merck, Germany), purity 99.8 %. The chemical shifts are referred to tetramethylsilane (TMS, $\delta_H$ = 0.00 ppm) in $CDCl_3$.

### *Synthetic procedures*

*Methyl α-D-glucopyranoside (1)*. Methyl *α*-D-glucopyranoside (**1**) was synthesized from *α*-D-glucose using Fisher glycosidation method with methanolic HCl, where the formation of the thermodynamically favoured pyranoside was achieved with a prolonged reaction time and refluxing.[13] In total, it was obtained 25.1 g methyl *α*-D-glucopyranoside (**1**), starting from 50 g

(0.2775 mol) *α*-D-glucose. The yield was 46.58 %. M.p. 164–165 °C. The melting point was in accordance with the previously reported data.[14]

*Methyl (*R*)-4,6-*O*-benzylidene-α-D-glucopyranoside (2)*. Methyl (*R*)-4,6-*O*-benzylidene--*α*-D-glucopyranoside (**2**) was synthesised using the procedure reported by Hall,[15] starting from 16.5 g (0.121 mol) anhydrous $ZnCl_2$, 25 mL (0.2462 mol) benzaldehyde ($\rho$ = 1.045 g/mL) and 16.5 g (0.0851 mol) powdered methyl *α*-D-glucopyranoside (**1**). The crude product was recrystallized with the optimal quantity of hot ethanol 14.15 g methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**2**, yield 59 %), were obtained, m.p. 165 °C. The reported melting point was in accordance with the previously published. [15-17]

*Methyl 4-O-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside (3)*. Methyl 4-*O*-benzoyl-6--bromo-6-deoxy-*α*-D-glucopyranoside (**3**) was prepared according to the modified Hanessian's procedure[18] starting from 0.910 g (3.22 mmol) methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**2**), 0.364 g (1.84 mmol) $BaCO_3$ and 0.6825 g (3.83 mmol) *N*-bromosuccinimide (NBS) and using dichloromethane as a solvent, instead of 1,1,2,2-tetrachloroethane. The obtained crystals had m.p. 121–122 °C, which is in accordance with the previously published value.[18] The obtained substance was chromatographed on a silica-gel column using the eluent chloroform:methanol = 15:1, and pure methyl 4-*O*-benzoyl-6-bromo-6-deoxy-*α*-D-glucopyranoside (**3**) was obtained with the mass 0.73 g, yield 65.68 %.

*Methyl 4-O-benzoyl-6-bromo-2-O-tert-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (4) and methyl 4-O-benzoyl-6-bromo-3-O-tert-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (5)*. The synthesis of compounds **4** and **5** started from 0.73 g (2.02 mmol) methyl 4-*O*-benzoyl-6--bromo-6-deoxy-*α*-D-glucopyranoside (**3**) and pyridine. They were put in round bottomed flask and stirred by hand until the complete dissolution of the carbohydrate derivative. The flask with the solution was left to cool down at 0 °C, and then 0.448 g (2.97 mmol) of TBDMSCl was added into the previously dissolved substance and cooled at 0 °C. The reaction mixture was left at room temperature for 8 days and followed using TLC with the mobile phase chloroform:methanol = 15:1. The reaction was terminated by the evaporation of pyridine on vacuum evaporator using ethanol. The oil thus obtained was eluted on silica gel column with the mixture chloroform:methanol = 40:1. In this way three reaction products were separated: methyl 4-*O*-benzoyl-6-bromo-2-*O*-tert-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**4**, 150 mg, 15.42 %; $^1$H-NMR spectrum along with the assignment is available in the Supplementary material to this paper, Fig. S-1), methyl 4-*O*-benzoyl-6-bromo-3-*O*-tert-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**5**, 180 mg, 18.51 %) and methyl 4-*O*-benzoyl-6--bromo-6-deoxy-2,3-di-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranoside (50 mg, 4.1 %).

*Methyl 4-O-benzoyl-6-bromo-2-O-tert-butyldimethylsilyl-6-deoxy-3-O-mesyl-α-D-glucopyranoside (6)*. 150 mg (0.32 mmol) of methyl 4-*O*-benzoyl-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**4**) was placed in round bottomed flask (100 mL) and dissolved in pyridine, and then cooled in ice bath to 0 °C, and then 0.06 mL (0.7752 mmol) methanesulfonyl chloride ($\rho$ = 1.48 g/mL) was added. The obtained mixture was left at 0 °C for 24 h. The reaction was monitored using TLC and terminated by the addition of a small quantity of water. Pyridine from the reaction mixture was removed by the co-evaporation with ethanol, and obtained oil was put on the silica gel column and eluted using chloroform. The mass of the obtained substance **6** was 60 mg (34.36 %). $^1$H-NMR spectrum and the assignments are available in the supplementary material (Fig. S-2).

*Methyl 4-O-benzoyl-6-bromo-3-O-tert-butyldimethylsilyl-6-deoxy-2-O-mesyl-α-D-glucopyranoside (7)*. 180 mg (0.38 mmol) methyl 4-*O*-benzoyl-6-bromo-3-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**5**) was put in the round bottom flask (100 mL) and dis-

solved in pyridine, then cooled in ice bath to 0 °C and methanesulfonyl chloride (0.06 mL, 0.7752 mmol) was added. The obtained mixture was left at 0 °C for 24 h. The reaction was monitored using TLC and interrupted by the addition of small quantity of water. Pyridine was removed from the reaction mixture by co-evaporation with ethanol, and the obtained oil was put on silica gel column and eluted using chloroform. The mass of the obtained substance **5** was 80 mg (38.18 %).

*Methyl 3,4-anhydro-6-bromo-2*-O-tert-*butyldimethylsilyl-6-deoxy*-α-*D-allopyranoside (**8**)*. Methyl 4-*O*-benzoyl-6-bromo-3-*O-tert*-butyldimethylsilyl-6-deoxy-2-*O*-mesyl-*α*-D-glucopyranoside (**7**) was put in the round bottomed flask (100 mL), and the same operation was performed for methyl 4-*O*-benzoyl-6-bromo-2-*O-tert*-butyldimethylsilyl-6-deoxy-3-*O*-mesyl-*α*-D-glucopyranoside (**6**). Ethanol was added to both flasks, in the quantity to dissolve the substance, and into thus obtained solutions 0.06 g (1.0693 mmol) KOH was added. The reaction was heated for 15 min at 70 °C which is enough time for the reaction to proceed quantitatively; it was monitored using TLC and chloroform as the mobile phase. Only one of those two makes epoxide, and it is the compound methyl 4-*O*-benzoyl-6-bromo-2-*O-tert*-butyldimethylsilyl-6--deoxy-3-*O*-mesyl-*α*-D-glucopyranoside (**6**), because it possesses good leaving group in the position 3, and the proof for it is TLC and the recorded $^1$H-NMR spectrum (Supplementary material, Fig. S-3). The mass of the obtained epoxide (methyl 3,4-anhydro-6-bromo-2-*O-tert*--butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside, **8**) is 30 mg (yield 78 %).

## RESULTS AND DISCUSSION

The anhydrous glucose was used as a starting material which was transformed into methyl *α*-D-glucopyranoside (**1**) using dry, gaseous HCl. Reaction was performed in a such a way that 50 g anhydrous glucose was refluxed for 72 h giving after cooling pure crystalline methyl *α*-D-glucopyranoside (**1**, m.p. 164 °C, Fig. 1). Yield of the first harvest was 16.5 g. The filtrate was evaporated to half volume after the filtering of crystals and left to stay in the fridge overnight. The obtained crystals were filtered and dried; 8.6 g methyl *α*-D-glucopyranoside (**1**) was obtained in the second harvest. Total yield of this reaction was 46.58 %.

Thus obtained methyl *α*-D-glucopyranoside (**1**) was treated with benzaldehyde in the presence of $ZnCl_2$, as a Lewis acid giving methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**2**, Fig. 1). The procedure was performed according to the instructions from Hall's method,[15] according to which it was firstly formed the complex between anhydrous $ZnCl_2$ and benzaldehyde, and then methyl *α*-D--glucopyranoside was added. The yields were different in this reaction and depended obviously on the purity of benzaldehyde, the presence of moisture in obtained methyl *α*-D-glucopyranoside, the heating and the presence of moisture in $ZnCl_2$. Therefore, to get yields around 65 % it is necessary each component to be maximally clean and dry.

The obtained methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**2**) was treated with *N*-bromosuccinimide (NBS) in dichloromethane in the presence of $BaCO_3$.[19] This reaction is very useful and important because the inactive benzylidene acetal in the position 6 was replaced by Br group in one step, which is easily reduced in the necessary $CH_3$ group, and the alkaline labile benzoyl group

remained in the position 4. Using the alkaline hydrolysis of benzoyl group obtained alkoxide ion easily closes epoxide of *allo*-configuration taking out *trans*-3-*O*-mesyl group. The reaction was performed in such a way that 0.91 g (3.22 mmol) methyl (*R*)-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**2**) was treated with 0.6825 g freshly prepared NBS in 35 mL dichloromethane previously dried through $Al_2O_3$ column. $BaCO_3$ was also added into the reaction (0.364 g, 1.84 mmol). The mixture was refluxed with stirring for 2.5 h and followed the changes using TLC. After the completion of the reaction, the insoluble $BaCO_3$ was filtered off and separated and after the evaporation of the solvent the oil was obtained. After the silica-gel chromatography methyl 4-*O*-benzoyl-6-bromo-6--deoxy-*α*-D-glucopyranoside (**3**) was obtained as a solid, yield 65.68 % (Fig. 1). Its melting point was in good agreement with the reported values.[18]

In the next step, the obtained compound was treated with TBDMSCl in pyridine, in a way that the compound was dissolved in pyridine, cooled at 0 °C in ice bath, and then TBDMSCl was added in a ratio 1.4 mol TBDMSCl to 1 mol of the compound. Three products were obtained: methyl 4-*O*-benzoyl-6-bromo-2-*O*--*tert*-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**4**), methyl 4-*O*-benzoyl--6-bromo-3-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-glucopyranoside (**5**), and methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2,3-di-*O*-*tert*-butyldimethylsilyl-*α*-D-glucopyranoside (Fig. 1). This mixture of products was separated on silica-gel column using the eluent chloroform:methanol = 40:1.

Both monosilyl derivatives were mesylated. To the cooled pyridine solution of silyl derivatives, mesyl chloride was added in a ratio 2.4 mol mesyl chloride to 1 mol silyl substrate. The reaction mixture was left at 0 °C for 24 h, and then upon the completion of the reaction, which flow was monitored using TLC, the obtained products (**6** and **7**) were isolated and separated on a silica gel column using chloroform as an eluent.

The structure of these two compounds was not checked because in the next step by the treatment with the base, the compound having TBDMS in position 3, cannot close the epoxide upon the attack of the alkoxide ion in position 4, and only the hydrolysis of benzoyl group takes place. Another compound having OMs group in the position 3 after hydrolysis closes into the 3,4-epoxide ring with *allo*-configuration (**8**, Fig. 1). This compound was characterized using $^1$H-NMR which spectrum is available in the Supplementary material (Fig. S-3). The simulated $^1$H-NMR spectrum of the same compound using NMRium[20] is also available in the Supplementary material (Fig. S-4), which was useful during the assignment process.

Earlier, based on *in vivo* studies, epoxides were considered to possess toxicity and poor pharmacokinetics.[21] However, the recent studies on compounds, such as fosfomycin (an antibiotic for the treatment especially of lower urinary tract infections), carfilzomib (an anti-cancer medication), fumagillin (an antimicrobial

agent) and TNP-470 (an anti-cancer candidate), clearly showed the role of the epoxide moiety in drug potency.[22] The obtained epoxide derivative can be used, therefore, as an intermediary in the syntheses of biologically active molecules.

## CONCLUSION

Epoxide derivatives are stable, but sufficiently reactive compounds to be used as intermediaries in syntheses. The synthesis of the epoxide derivative (methyl 3,4-anhydro-6-bromo-2-*O*-*tert*-butyldimethylsilyl-6-deoxy-*α*-D-allopyranoside) from a cheap starting material (*α*-D-glucose) was achieved in a high yield and the by minimal number of synthetic steps.

## SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12572, or from the corresponding author on request.

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## ИЗВОД

## СИНТЕЗА МЕТИЛ 3,4-АНХИДРО-6-БРОМО-2-*O*-*ТЕРЦ*-БУТИЛДИМЕТИЛСИЛИЛ-6-ДЕОКСИ-*α*-D-АЛОПИРАНОЗИДА ИЗ *α*-D-ГЛУКОЗЕ

ЂОРЂЕ ГЛИШИН, ОЛГА ЈОВАНОВИЋ, ГОРДАНА СТОЈАНОВИЋ, АЛЕКСАНДРА ЖИВКОВИЋ, ДРАГАН СТОЈАНОВИЋ, МАРИНА ПАВЛОВИЋ и БИЉАНА АРСИЋ

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Неки једноставни угљени хидрати и њихови деривати се користе клинички у третману различитих болести. Епоксидни деривати, који се могу добити интрамолекулском елиминацијом воде из две вициналне хидроксилне групе су стабилна, али довољно реактивна једињења која се често користе као интермедијери у различитим синтезама. Синтеза епоксидног деривата, метил 3,4-анхидро-6-бромо-2-*O*-*терц*-бутилдиметилсилил-6-деокси-*α*-D-алопиранозида из *α*-D-глукозе је остварена у високом приносу у минималном броју синтетичких корака. Анхидрована глукоза је коришћена као полазни материјал који је трансформисан у метил-*α*-D-глукопиранозид коришћењем сувог, гасовитог хлороводоника. Тако добијени дериват је третиран са бензалдехидом у присуству цинк хлорида као Луисове киселине дајући метил-(*R*)-4,6-*O*-бензилиден-*α*-D-глукопиранозид. Добијено једињење је третирано са *N*-бромсукцинимидом (NBS) у дихлорметану у присуству баријум-карбоната дајући метил-4-*O*-бензоил-6-бромо-6-деокси-*α*-D-глукопиранозид. У следећој фази добијено једињење је третирано са *терц*-бутилдиметилсилил-хлоридом (TBDMSCl) у пиридину, и метил 4-*O*-бензоил-6-бромо-2-*O*-*терц*-бутилдиметилсилил-6-деокси-*α*-D-глукопиранозид је даље мезилован, и добијени метил-4-*O*-бензоил-6-бромо-2-*O*-*терц*-бутилдиметилсилил-6-деокси-3-*O*-мезил-*α*-D-глукопиранозид

је третиран са KOH на крају, дајући метил-3,4-анхидро-6-бромо-2-*O*-*трет*-бутилдиметилсилил-6-деокси-*α*-D-алопиранозид (принос 78 %).

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