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# Preparation of Versatile Synthetic Precursors of Optically Active 5a-Carbasugars from (–)-*vibo-*Quercitol

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The spiro-epoxide derived from (-)-2-deoxy-scyllo-inosose was converted into the iodide **2**, which was directly subjected to elimination conditions, affording the key methylene compound **4**. Successive cyclohexylidenation of the tetrol obtained from **4**, selective benzoylation, and conventional tosylation gave the homoallyl tosylate **11**, which would be a versatile intermediate for preparation of biologically active 5a-carbahexopyranosylamines and their unsaturated congeners.

Keywords Cyclitols, Inositols, Bioconversion, Carbohydrate mimics, Carba-sugars, Carba-glycosylamines

## INTRODUCTION

We have been engaged in developing effective routes to connect readily available myo-inositol to optically active carba-sugars<sup>[1]</sup> of biologic interest. Practically, a number of carba-glycosylamines can be furnished<sup>[2]</sup> by chemical

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degradation and/or biogenesis of antibiotic validamycins. In recent years optically active carba-sugars have been totally synthesized<sup>[3]</sup> starting from common hexopyranose derivatives, (-)-shikimic acid, and so on. However, no process has been successfully employed for the production of large quantities of desired carba-sugars.

In a preceding paper,<sup>[4]</sup> we documented transformation of (-)-2-deoxyscyllo-inosose derived by bio-oxidation of (-)-vibo-quercitol<sup>[5]</sup> into a single crystalline spiroepoxide, from which (-)- $\beta$ -valiol<sup>[6]</sup> and clinically important (-)-valiolamine<sup>[7]</sup> were prepared, thus establishing a link between cyclitols and chiral carba-sugars. This process might also be applicable for provision of branched-chain cyclitol derivatives and carba-sugars.

We report here ready synthesis of a key intermediate, 1L-(1,3/2,4)-5methylene-1,2,3,4-cyclohexanetetrol (2,3,4-tri-O-acetyl-5-deoxy-5a-carba- $\beta$ -Dxylo-5-enopyranose acetate)<sup>[8]</sup> (4), to provide 5a-carba-hexopyranoses as well as valienamine type unsaturated 5a-carba-hexopyranosylamines<sup>[9,10]</sup> of biological importance (Sch. 1).



**Scheme 1:** Synthetic routes to biologically interesting 5a-carba-sugar derivatives from *myo*-inositol.

## **RESULTS AND DISCUSSION**

Conversion of the spiro-epoxide<sup>[4]</sup> into the *exo*-methylene compound **4** was attempted through an elimination reaction of the halides obtained from it (Sch. 2). Thus, treatment of the epoxide with 20% HBr-AcOH at 50°C gave the 7-bromide **1** selectively in 80% yield, which was then subjected to conventional elimination conditions<sup>[11]</sup> with zinc powder in refluxing acetic acid. However, a major product was shown to be penta-*O*-acetyl-(–)- $\beta$ -valiol **3** (58%), resulting from substitution at C-7 with an acetate ion. Alternatively, the epoxide was treated with concd. hydroiodic acid in acetic acid at rt to give the iodide **2** (~100%). Interestingly, under similar elimination conditions as above, compound **2** was converted into the desired *exo*-methylene compound **4** preferentially in 85% yield. The structure of **4** was confirmed by its <sup>1</sup>H NMR spectrum, with signals due to H-4 and H-5a protons as a doublet (J = 9.8 Hz)



**Scheme 2:** Synthesis of the key intermediates **4** and **11** from the spiro-epoxide. Conditions and reagents: (a) 20% HBr-AcOH, 50°C ( $\rightarrow$  **1**); HI (2 molar equiv.), AcOH, r.t. ( $\rightarrow$  **2**); (b) Zn powder, AcOH, 2 hr, reflux temp; (c) NaOMe, MeOH;  $\alpha$ ,  $\alpha$ -dimethoxycyclohexane ( $\sim$ 10 molar equiv.), TsOH  $\cdot$  H<sub>2</sub>O (0.2 molar equiv.), DMF, 8 hr, rt; (d) Ac<sub>2</sub>O, pyridine, rt; (e) benzoic acid (1.2 molar equiv.), Et<sub>3</sub>N (1.2 molar equiv.), EDC  $\cdot$  HCI (1.2 molar equiv.), DMAP (0.2 molar equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 2 days, rt; (f) TsCl, DMAP, pyridine.

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and two resonated doublets of doublets (J = 5.4, 13.2 Hz and J = 11.7, 13.2 Hz) at  $\delta$  5.39, 2.82, and 2.25, respectively.

Compound 4 was O-deacetylated with methanolic sodium methoxide, and the resultant tetrol was allowed to react with 1,1-dimethoxycyclohexane (23 molar equiv.) in DMF in the presence of TsOH · H<sub>2</sub>O (0.2 molar equiv.) at rt to give, after fractionation over a column of silica gel, the 1,2-, 2,3-, and 3,4-O-cyclohexylidene derivatives<sup>a</sup> **5a**, **6a**, and **7a** in 13%, 53%, and 17% yields, respectively. Their structures were clearly established on the basis of <sup>1</sup>H NMR spectral data of their respective di-O-acetyl derivatives **5b**, **6b**, and **7b**. For example, the structure of **6b** was assigned on the basis of its spectrum, which indicated signals due to H-1 and H-4 as a doublet of doublets of doublets (J = 5.4, 9.9, 10.0 Hz) and a doublet (J = 10.5 Hz) at  $\delta$  4.86 and 5.41, respectively. Practically, the tetrol obtained by hydrolysis of compounds **5a** and **7a** was again subjected to cyclohexylidenation conditions to improve the yield of **6a**.

Next, selective benzoylation of **6a** was attempted by treatment with benzoic acid (1.2 molar equiv.) in the presence of 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide hydrochloride (EDC · HCl, 1.2 molar equiv.), Et<sub>3</sub>N (1.2 molar equiv.), and DMAP (0.2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> for two days at  $-30^{\circ}$ C to room temperature to afford, after fractionation over a silica gel column, the 1-O-, 4-O-, and 1,4-di-O-benzoyl derivatives **8**, **9**, and **10** in 13%, 35%, and 27% yields, respectively. On conventional tosylation, the major benzoate **9** was converted into reactive intermediate tosylate **11** (~100%), the structure of which was established by its <sup>1</sup>H NMR spectrum, exhibiting a signal due to H-4 as a doublet (J = 10.6 Hz) at  $\delta$  5.62. This compound is equivalent to the corresponding 1-bromide that was effectively utilized<sup>[12]</sup> as the intermediate for preparation of  $\beta$ -valienamine and its 4-epimer. To improve the practical yield of **9**, compounds **8** and **10** were readily convertible into **6a** by *O*-debenzoylation with MeONa in MeOH.

Reactivity of the homoallyl tosylate **11** toward common nucleophiles was first studied to assess reaction conditions to facilitate elimination and/or substitution reactions as selectively as possible (Sch. 3). Treatment of **11** with a large excess of lithium chloride (30 molar equiv.) in DMF in the presence of triethylamine was carried out at 85°C to afford the chloride **12** (62%) and the elimination product **14** (15%). The structure of the chloride **12** was assigned by the <sup>1</sup>H NMR signals for H-2 and H-3 at  $\delta$  3.58 and 4.25 as doublets of doublets (J = 3, 9.5 Hz) and (J = 9.5, 10.3 Hz), respectively. The structure of the alkadiene **14** was also assigned by the <sup>1</sup>H NMR spectrum, which contained a doublet (J = 8.4 Hz) and a doublet of doublets (J = 8.4, 11.2 Hz) at  $\delta$  4.43 and 3.93 due to H-2 and H-3 signals, respectively. Alternatively, azidolysis of **11** with 10 molar equiv. of sodium azide in DMF at 85°C produced the  $\alpha$ -azide **13** (77%)

<sup>&</sup>lt;sup>a</sup>All compounds **4–14** are designated the derivatives of 5a-carba-hexopyranose.



Scheme 3: Reactions of the tosylate 11. Conditions and reagents: (a) LiCl (30 molar equiv.), Et<sub>3</sub>N, DMF, 85°C (11  $\rightarrow$  12); NaN<sub>3</sub> (10 molar equiv.), DMF, 85°C (11  $\rightarrow$  13).

along with 14 (12%). The <sup>1</sup>H NMR spectrum of 13 contained two resonated doublets of doublets at  $\delta$  3.86 (J = 2.7, 9.3 Hz) and 4.14 (J = 9.3, 10.4 Hz), attributable to H-2 and H-3, confirming the assigned structure. These results indicated 11 as a nice candidate for direct nucleophilic substitution at C-1. Compound 12 is considered to be equivalent to the  $\alpha$ -anomer of 11, which would produce the  $\beta$ -azide by azidolysis. All reaction conditions have not been optimized yet. The alkadiene 14, obtainable mainly by treatment of 11 with DBU in toluene, offered a key intermediate<sup>[13]</sup> for preparation of  $\beta$ -valienamine derivatives. Selected <sup>1</sup>H NMR data for key compounds are presented below.<sup>b</sup>

Recently, the 1L-(1,2/3,4)-isomer of 5-methylene-1,2,3,4-cyclohexanetetrol was prepared<sup>[14]</sup> from a D-mannitol derivative through a multistep sequence and demonstrated to be utilized as a versatile intermediate for preparation of 5a-carbafucopyranose. In conclusion, the optically active 1L-(1,3/2,4)-isomer

<sup>&</sup>lt;sup>b</sup>Specific rotations and <sup>1</sup>H NMR data follow **4**:  $[\alpha]_{D}^{22} = +5.5^{\circ}$  (c = 1.8, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CDCl}_3): \delta 5.39 \text{ (d, 1H, } J_{3,4} 9.8 \text{ Hz}, \text{ H-4}), 5.28 \text{ (dd, 1H, } J_{1,2} = J_{2,3} 9.8 \text{ Hz}, \text{ H-2}),$ 5.05 (m, 3H, H-3, 2 × H-6), 4.82 (ddd, 1H,  $J_{1,5a(eq)}$  5.4 Hz,  $J_{1,2}$  9.8 Hz,  $J_{1,5a(ax)}$  11.7 Hz, H-1), 2.82 [dd, 1H,  $J_{1,5a(eq)}$  5.4 Hz,  $J_{5agem}$  13.2 Hz, H-5a(eq)], 2.25 (dd, 1H,  $J_{1,5a(ax)}$  11.7 Hz,  $J_{5agem}$  13.2 Hz, H-5a(ax)], 2.12, 2.03, 2.02, 2.01 (4 s, each 3H, 4 × OAc). **6b**:  $[\alpha]_{D}^{22} = -27^{\circ}$  $(c = 0.52, \text{CHCl}_3)$ ; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  5.41 (d, 1H,  $J_{3,4}$  10.5 Hz, H-4), 5.08, 4.95  $(2 \text{ s, each 1H}, 2 \times \text{H-6}), 4.86 \text{ (ddd, 1H}, J_{1,5a(eq)} 5.4 \text{ Hz}, J_{1,2} 9.9 \text{ Hz}, J_{1,5a(ax)} 10.0 \text{ Hz}, \text{H-1}),$  $3.76 \,(\mathrm{dd}, \, 1\mathrm{H}, \, J_{2,3} \, 9.3 \,\,\mathrm{Hz}, \, J_{1,2} \, 9.9 \,\mathrm{Hz}, \,\mathrm{H-2}), \, 3.48 \,(\mathrm{dd}, \, 1\mathrm{H}, \, J_{2,3} \, 9.3 \,\,\mathrm{Hz}, \, J_{3,4} \,\, 10.5 \,\mathrm{Hz}, \,\mathrm{H-3}),$ 2.92 [dd, 1H,  $J_{1,5a(eq)}$  5.4 Hz,  $J_{5agem}$  13.9 Hz, H-5a(eq)], 2.14 [m, 1H, H-5a(ax)], 2.21, 2.11 (2 s, each 3H, 2 × OAc), 1.67 (m, 10 H, C<sub>6</sub>H<sub>10</sub>). **11** [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -15° (c = 2.8, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CDCl}_3): \delta 8.12 - 7.26 \text{ (m, 9 H, Ph)}, 5.62 \text{ (d, 1H, } J_{3.4} \text{ 10.6 Hz}, \text{H-4}), 5.11, 5.05 \text{ (2 s, 10.1 m)}, 5.05$ each 1H, 2 × H-6), 4.57 (ddd, 1H,  $J_{1,5a(eq)}$  5.4 Hz,  $J_{1,2}$  9.8 Hz,  $J_{1,5a(ax)}$  10.3 Hz, H-1), 3.74  $(\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{1,2}\,9.6\,\mathrm{Hz},\,\mathrm{H-2}),\,3.51\,(\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{3,4}\,10.6\,\mathrm{Hz},\,\mathrm{H-3}),\,3.01\,[\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{3,4}\,10.6\,\mathrm{Hz},\,\mathrm{H-3}),\,3.01\,[\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{3,4}\,10.6\,\mathrm{Hz},\,\mathrm{H-3}),\,3.01\,[\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{3,4}\,10.6\,\mathrm{Hz},\,\mathrm{H-3}),\,3.01\,[\mathrm{dd},\,1\mathrm{H},\,J_{2,3}\,9.3\,\mathrm{Hz},\,J_{3,4}\,10.6\,\mathrm{Hz},\,\mathrm{H-3}),\,3.01\,[\mathrm{dd},\,1\mathrm{Hz},\,\mathrm{HZ},\,\mathrm{HZ$ CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.16 (m, 2 H, Ph), 7.54 (m, 3H, Ph), 5.65 (d, 1H, J<sub>3,4</sub> 10.4 Hz, H-4), 5.09 (br s, 2 H, 2  $\times$  H-6), 4.29 (m, 1H, H-1), 4.14 (dd, 1H,  $J_{2,3}$  9.3 Hz,  $J_{3,4}$ 10.4 Hz, H-3), 3.86 (dd, 1H,  $J_{1,2}$  2.7 Hz,  $J_{2,3}$  9.3 Hz, H-2), 2.54 [m, 2 H, H-5a(ax), H-5a(eq)], 1.71 (m, 10 H, C<sub>6</sub>H<sub>10</sub>). **14**:  $[\alpha]_D^{20} = +47^{\circ}$  (c = 0.13, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ 8.14 (m, 2 H, Ph), 7.62–7.45 (m, 3H, Ph), 6.13 (m, 3H, H-1, H-4, H-5a), 5.25, 5.12 (2 s, each 1H, 2 × H-6), 4.43 (d, 1H,  $J_{2,3}$  8.4 Hz, H-2), 3.93 (dd, 1H,  $J_{2,3}$  8.4 Hz,  $J_{3,4}$  11.2 Hz, H-3), 1.64 (m, 10 H, C<sub>6</sub>H<sub>10</sub>).

**4**, obtained directly from *myo*-inositol through bioconversion combined with conventional synthetic procedures, promises to be a key compound convertible to quantities of optically pure carba-sugars, allowing us readily to design and synthesize biologically active carba-sugar derivatives with ease.

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