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Transformation of Sugars to Chiral Polyols over a Heterogeneous Catalyst

Masazumi Tamura*, Naoto Yuasa, Ji Cao, Yoshinao Nakagawa and Keiichi Tomishige*

Abstract: Transformation of sugars with maintaining the intrinsic stereostructure is desirable to make full use of sugars, however, there is no choice but to use multistep synthesis with protection and deprotection of the OH groups due to the similar reactivities of the OH groups. Herein, a new method for selective transformation of sugar derivatives to chiral building blocks and a diol synthon with retention of the intrinsic configuration (stereo- and regioselectively) is demonstrated. The key to the success is based on the selective recognition of *cis*-vicinal OH groups in sugars and one-pot simultaneous removal of the *cis*-vicinal OH groups to the dideoxy sugars without protection of OH groups except the OH group of the hemiacetal group over heterogeneous CeO_2-supported ReO_x and Pd (ReO_x-Pd/CeO_2) catalyst by using H_2 as a reducing agent.

Biomass is a promising renewable resource which can replace fossil fuels because biomass is an only organic resource among various renewable ones. Sugars are main frameworks of biomass, and it is greatly desirable to develop an innovative and effective method for transformation of biomass-derived sugars to valuable chemicals on the background of resource depletion and global climate change.

Selective transformation of sugars requires selective dissociation of the C-O or C-C bonds, and it has been intensively investigated with homogeneous, heterogeneous, and enzymatic catalysts[1-3]. The most typical method for the transformation of sugars is via formation of furfural and 5-hydroxymethyl furfural because the furfurals can be easily produced by dehydration of sugars in the presence of acid catalysts (Scheme 1(C))[4-8]. The method via formation of sugar alcohols is also proposed by combination of aqueous-phase reforming, dehydration and/or hydrogenation (hydrogenolysis) to produce alkanes and alkanols[9,10]. However, such transformation methods lose the unique stereostructure of sugars. As for methods with retention of the stereostructure of sugars, biocatalytic transformation of sugars to chiral chemicals such as lactic acid is a well-known process, however artificial catalytic transformation is very limited. To our best knowledge, there are no reports on effective catalysts for the one-pot selective removal of one or some OH groups from unprotected sugars and sugar derivatives to produce deoxy sugars in spite that deoxy sugars form the main frameworks of natural products[11] and are used as a vital scaffold for medicines[12]. Conventionally, synthesis of deoxy sugars needs multistep synthesis with a technique of protection and deprotection, leading to low yield and high cost[11]. De novo synthesis method is also proposed as an alternative method for the synthesis of deoxy sugars[13], which however suffers from multistep synthesis, low yield and low availability of starting materials. Recently, Gagné and co-workers demonstrated an effective method for selective dissociation of C-O bonds in silyl-protected polyols to chiral polyol synthons with maintaining the stereocenters of polyols using $B(C_6F_5)_3$ and tertiary silane[14-16], however, the method required the silyl pre-protection of the OH groups and more than equivalent amount of silane additives. Therefore, catalytic and selective transformation of sugars without protection of OH groups to deoxy sugars with maintaining the original stereostructure by using cheap reductants such as H_2 is ideal.

For the purpose, selective recognition of one or some OH groups in sugars by catalysts is essential, and the unique cyclic stereostructure of sugars will give an opportunity for the selective recognition. However, the stability of the cyclic structure of sugars is generally not so high, and methyl glycosides are often used as synthons of sugars[17] because they have more stable cyclic structure and can be easily produced from sugars and methanol and restored to sugars. Hydrogenolysis of C-O bonds in methyl glycosides is one of the options for removal of the OH groups, however, selective hydrogenolysis of specific OH groups is so far quite difficult due to the similar characteristic of the OH groups, resulting in a variety of products (Scheme 1(A)). On the other hand, deoxydehydration (DODH) is well-known as a method for simultaneous removal of vicinal OH groups in polyols to olefin groups[18-24]. Recently, we found that a combination method of deoxydehydration-hydrogenation (DODH-HG) was effective for one-pot simultaneous removal of vicinal OH groups in diols to the corresponding dideoxy products[25,26]. In this method, CeO_2-supported ReO_x modified with Pd (ReO_x-Pd/CeO_2) was an efficient heterogeneous catalyst for the reaction by using gaseous H_2 as a reducing agent without dissociation of C-C bonds. The detailed roles of each metal species of ReO_x-Pd/CeO_2 in DODH reaction are shown in the supporting information. The method can largely decrease the number of products from sugars (Scheme 1(B)), and moreover focusing on the cyclic structure of methyl glycosides, recognition of only one of *cis*-vicinal or *trans*-vicinal OH groups by a catalyst will enable more selective transformation of sugars. Herein, we substantiated selective transformation of *cis*-vicinal OH groups in methyl glycosides to the dideoxy glycosides by selective recognition of *cis*-vicinal OH groups, and the produced dideoxy glycosides could be transformed to useful chemicals such as chiral building blocks and α,ω-diol synthons (Scheme 1(D)).

To clarify the potential of ReO_x-Pd/CeO_2 catalyst for selective removal of *cis*-vicinal or *trans*-vicinal OH groups, deoxydehydration-hydrogenation (DODH-HG) of methyl C6- and C5-glycosides with *cis*-vicinal or *trans*-vicinal OH groups was investigated as model substrates with ReO_x-Pd/CeO_2(Re:

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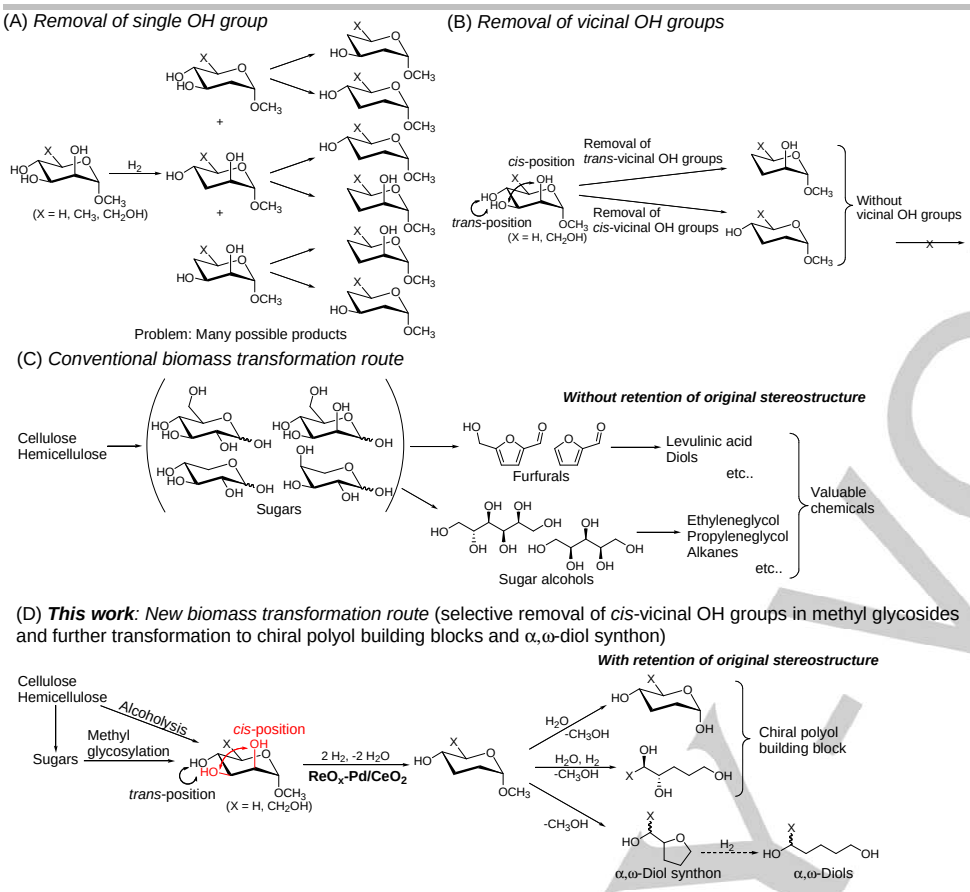
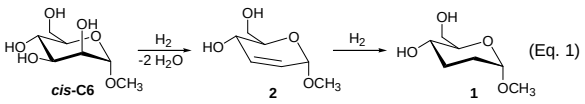


Scheme 1. Transformation methods of biomass-derived sugars and methyl glycosides.

2wt%, Pd/Re=1/4) catalyst, which is the optimized one in our previous work[25,26] (Figure 1). Methyl C6-glycoside with *cis*-vicinal OH groups, methyl α-D-mannopyranoside (***cis*-C6**), reacted to afford the corresponding dideoxy sugar, methyl α-D-2,3-dideoxy-mannopyranoside (**1**), with high selectivity (98%). On the other hand, methyl C6-glycoside without *cis*-vicinal OH groups, methyl α-D-glucopyranoside (***trans*-C6**), hardly reacted, and no target deoxyglycoside was obtained. In addition, the reaction with mixture of these C6-glycosides (***cis*-C6**+***trans*-C6**) showed that only ***cis*-C6** reacted in high selectivity (97%), while the conversion was decreased by the presence of ***trans*-C6**, which will be due to the competitive adsorption of ***trans*-C6** on the active site of ReO_x-Pd/CeO_2 catalyst. Similar tendency was observed in the case of methyl C5-glycosides, although the reactivity of methyl C5-glycoside with *cis*-vicinal OH groups, methyl β-D-ribofuranoside (***cis*-C5**), is higher than that of ***cis*-C6**. These results suggest that only *cis*-vicinal OH groups in sugars can be selectively removed even if other sugars with *trans*-vicinal OH groups coexist. In addition, to compare the reactivity between ***cis*-C6** and ***trans*-C6** more precisely, the reaction with ***trans*-C6** at longer reaction time of 24 h was carried out, providing 2% conversion and no target product. The reactivity of ***cis*-C6** is at least more than 100-fold higher than that of ***trans*-C6**, indicating that ReO_x-Pd/CeO_2 catalyst can selectivity recognize the structure of *cis*-vicinal OH groups to achieve highly selective removal of *cis*-vicinal OH groups in methyl glycosides.

The time-course of DODH-HG of methyl α-D-mannopyranoside (***cis*-C6**) over ReO_x-Pd/CeO_2 catalyst is shown in Figure 2. The conversion increased smoothly to reach >99% conversion at 51 h and the selectivity to **1** was 96%, providing **1** in 96% yield. The turnover frequency (TOF) and turnover number (TON) based on total Re amount were calculated to be 4.9 h^{-1} and 77, respectively by using the results at 0 and 4 h, and that at 51 h. The values were lower than the reported ones in the case of 1,4-anhydroerythritol (TOF=35 h^{-1}, TON=600) over the same catalyst at the same reaction temperature and H_2 pressure[25,26]. Particularly, the TOF was lower than those of 1,4-anhydroerythritol and simple diols[25,26], suggesting that the reactivity of methyl glycosides is low compared with simple diols. Focusing on the selectivity at the initial stage, methyl α-D-2,3-dideoxy-*erythro*-hex-2-enopyranoside (**2**) was observed and the selectivity decreased with increasing reaction time. These results suggest that the formation of **1** proceeds via hydrogenation of **2** and **2** is produced by DODH reaction of ***cis*-C6** (Eq. 1). At longer reaction time (95 h), the selectivity to **1** decreased and that to others including dehydration and/or hydrogenation products of **1** increased.

The reusability of ReO_x-Pd/CeO_2 catalyst was studied in the



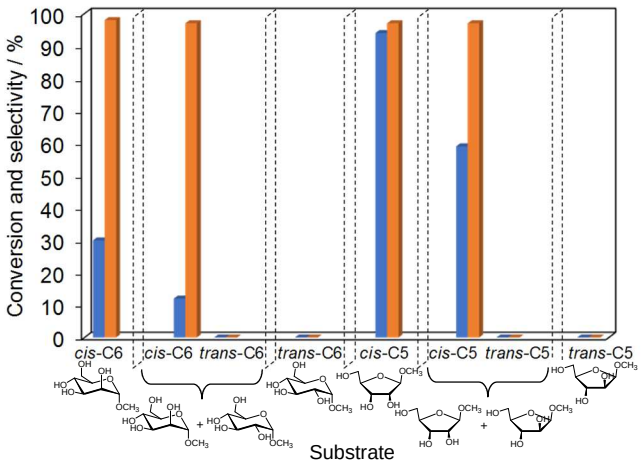


Figure 1. Comparison of reactivities of methyl glycosides with *cis*- or *trans*-vicinal OH groups over ReO_x–Pd/CeO_2 catalyst. Conversion (blue bar) and selectivity to the dideoxy sugars (orange bar) of various combination of methyl C6- and C5-glycosides with *cis*- and *trans*-vicinal OH groups. Reaction conditions: substrate 0.125 g or 0.125 + 0.125 g (for mixture substrate), 1,4-dioxane 10 g, ReO_x-Pd/CeO_2(Re: 2wt%, Pd/Re=1/4) 150 mg (100 mg for methyl C5-glycosides), 413 K, H_2 8 MPa, 1 h.

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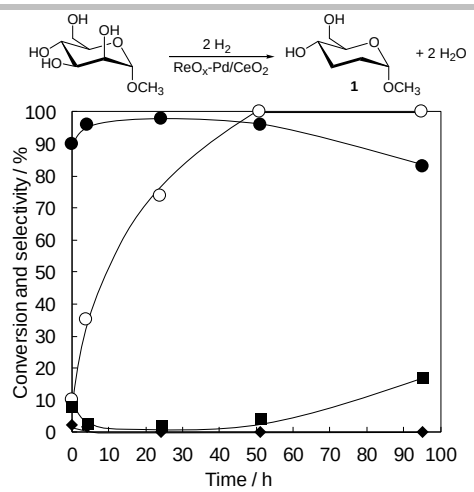
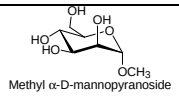
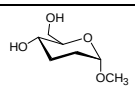
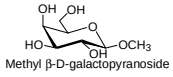
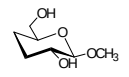
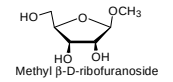
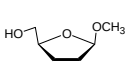
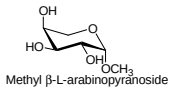
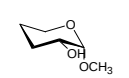
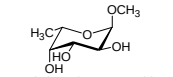
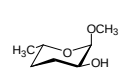
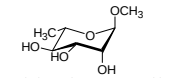
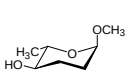


Figure 2. Time-course of DODH-HG of methyl α-D-mannopyranoside over ReO_x–Pd/CeO_2 catalyst (○: conversion, ●: selectivity to **1**, ◆: selectivity to **2**, ■: selectivity to others). Reaction conditions: methyl α-D-mannopyranoside 0.25 g, ReO_x–Pd/CeO_2(Re: 2wt%, Pd/Re=1/4) 150 mg, 1,4-dioxane 10 g, 413 K, H_2 8 MPa.

same reaction (Figure S1). The catalyst could be reused four times without loss of activity and selectivity. The structure of the catalyst was maintained after the reuse test, which was confirmed by XRD (Figure S2), XANES (Figure S3) and EXAFS (Figures. S4 and S5, and Tables S1 and S2) analyses. From the ICP analysis of the filtrate, the leaching amount of Pd and Re species was below the detection level and 1%, respectively. Therefore, ReO_x-Pd/CeO_2 is a reusable heterogeneous catalyst. The scope of methyl glycosides with *cis*-vicinal OH groups was investigated using ReO_x–Pd/CeO_2 catalyst (Table 1). The *cis*-vicinal OH groups in the methyl glycosides were selectively removed to afford the corresponding dideoxy glycosides in high yields with high selectivities by optimizing the catalyst amount and reaction time, and the yields were much higher than those in the previous reports (≤31% total yield of methyl-α-D-2,3-dideoxy mannopyranoside from D-glucose with 6 steps[27,28], 40% total yield of methyl-D-2,3-dideoxy riboside from halogenated benzene with 7 steps[29] and 54% total yield for methyl-β-D-3,4-dideoxy galactopyranoside from methyl β-D-galactopyranoside with 6 steps[30], Scheme S1). Judging from the optimized catalyst amount and reaction time, the reactivity of a methyl glycoside with a five-membered ring (entry 3) is higher than those with a six-membered ring. This is the first report on high-yield synthesis of dideoxy glycosides directly from methyl glycosides without protection of OH groups except the OH group of the hemiacetal group using H_2 as a reducing agent.

Table 1 Scope of methyl glycosides in DODH-HG over ReO_x–Pd/CeO_2 catalyst

Entry	Substrate	Product	Catalyst amount /mg	*t* /h	Conv. /%	Sel. /%	Yield[a] /%
1	 Methyl α-D-mannopyranoside		150	51	99	97	96(91)
2	 Methyl β-D-galactopyranoside		300	72	94	94	88(84)
3	 Methyl β-D-ribofuranoside		100	24	>99	94	93(93)
4	 Methyl β-L-arabinopyranoside		150	72	>99	93	93(88)
5	 Methyl α-L-fucopyranoside		450	95	97	83	82(78)
6	 Methyl α-L-rhamnopyranoside		150	36	>99	92	92(87)

Reaction conditions: methyl glycoside 0.25 g, ReO_x–Pd/CeO_2(Re=2 wt%, Pd/Re=1/4), 1,4-dioxane 10 g, 413 K, H_2 8 MPa. [a]The numbers outside and inside the parentheses are GC and isolated yields, respectively.

To expand the application of the method, further transformation of the produced dideoxy glycoside to valuable chemicals was investigated using methyl β-D-ribofuranoside as a model substrate (Scheme 2(A)). After the DODH-HG of methyl β-D-ribofuranoside, ReO_x-Pd/CeO_2 was removed by filtration, and the produced dideoxy glycoside was easily transformed to the corresponding dideoxy ribofuranose in high yield of 97% only by addition of H_2O under the conditions of 393 K and 4 h (hydration, Scheme 2(A)-(a)). On the other hand, after the DODH-HG, water was added to the reaction mixture without removal of ReO_x-Pd/CeO_2 catalyst and the mixture was reacted at 393 K in 1,4-dioxane for 48 h, providing the (2*S*)-1,2,5-pentanetriol in high yield of 97% and high ee of 96% with maintaining the configuration of the original methyl β-D-ribofuranoside (hydration+hydrogenation, Scheme 2(A)-(b)). In addition, after the DODH-HG, ReO_x-Pd/CeO_2 was removed by filtration, and Rh-ReO_x/SiO_2 and *n*-heptane were added into the filtrate and the mixture was heated under H_2 at 393 K for 24 h, providing tetrahydrofurfuryl alcohol (THFA) in high yield of 91% (Scheme 2(A)-(c)), which will be produced by the consecutive reactions of hydration, hydrogenation and dehydration (Scheme S2). Considering that THFA can be easily transformed by hydrogenolysis to 1,5-pentanediol in high yield (up to 94%) over Rh-ReO_x or Ir-ReO_x catalysts[31,32], the transformation route can be a new production process of α,ω-diols such as 1,5-pentanediol and 1,6-hexandiol from biomass. In contrast, (2*R*)-1,2,5-pentanetriol was also obtained in high yield of 95% and high ee of 95% with maintaining the configuration of the original structure from methyl β-L-arabinopyranoside via DODH-HG over ReO_x-Pd/CeO_2 catalyst, and subsequent hydration and hydrogenation over Rh-ReO_x/SiO_2 catalyst (Scheme 2(B)). Therefore, enantiomers of 1,2,5-pentanetriol could be individually synthesized from glycosides by changing the starting materials.

Finally, one-pot transformation of D-ribose to (2*S*)-1,2,5-pentanetriol was demonstrated by combination of catalysts (Scheme 2(C)). D-Ribose easily underwent glycosylation by methanol at room temperature under air with Ir-ReO_x/SiO_2 catalyst to provide mixture of methyl β-D-ribofuranoside and methyl α-D-ribofuranoside (79% and 19%). After the reaction, ReO_x-Pd/CeO_2 was added into the reaction mixture without removal of Ir-ReO_x/SiO_2 catalyst, and the mixture was reacted at 413 K under H_2 for 4 h, providing the corresponding dideoxy glycosides in 95% yield (methyl β-D-2,3-dideoxy-ribofuranoside

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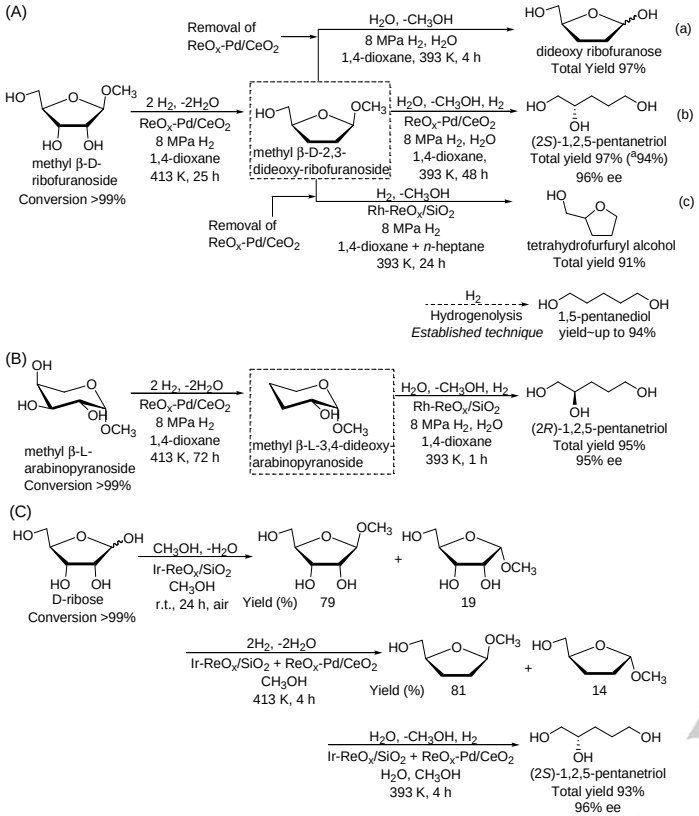

Scheme 2. Synthesis of chiral building blocks and α,ω-diol synthon. (A) Formation of dideoxy ribofuranose, (2*S*)-1,2,5-pentanetriol and tetrahydrofurfuryl alcohol from methyl β-D-ribofuranoside. (B) Formation of (2*R*)-1,2,5-pentanetriol from methyl β-L-arabinopyranoside. (C) Formation of (2*S*)-1,2,5-pentanetriol from D-ribose. See supplementary materials for detailed procedures.

81% + methyl α-D-2,3-dideoxy-ribofuranoside 14%). The produced reaction mixture with water was heated, affording (2*S*)-1,2,5-pentanetriol in 93% yield with 96% ee. This is first example of one-pot transformation of sugars to chiral alcohols in high yield and high ee without protection of OH groups except the OH group of the hemiacetal group.

In conclusion, we found that ReO_x-Pd/CeO_2 was an effective heterogeneous catalyst for the direct and selective transformation of methyl glycosides with *cis*-vicinal OH groups to dideoxy glycosides without protection of OH groups except the OH group of the hemiacetal group by deoxydehydration and subsequential hydrogenation using gaseous H_2 as a reductant. The key for the selective transformation is recognition of *cis*-vicinal OH groups in the methyl glycosides by ReO_x-Pd/CeO_2 catalyst, leading to selective conversion of the *cis*-vicinal OH groups to C=C bond by deoxydehydration. Various methyl glycosides with *cis*-vicinal OH groups were converted to the corresponding dideoxy glycosides in high isolated yields (78-93%) with maintaining the intrinsic structure. Furthermore, we demonstrated that the produced dideoxy glycoside can be selectively transformed to the chiral polyols in high yield and high ee by hydration and hydrogenation, and both enantiomers of 1,2,5-pentanetriol can be individually synthesized by changing the starting substrate of methyl glycosides. Tetrahydrofurfuryl alcohol, a diol synthon of 1,5-pentanediol, was also synthesized in high yield by hydration and hydrogenation of the produced dideoxy sugar. One-pot transformation of D-ribose to (2*S*)-1,2,5-pentanetriol was substantiated in high total yield (93%) and high ee (96%) by combination of ReO_x-Pd/CeO_2 and Ir-ReO_x/SiO_2 catalysts.

Keywords: Sugar, Deoxydehydration, hydrogenation, heterogeneous catalyst, Rhenium, Cerium oxide

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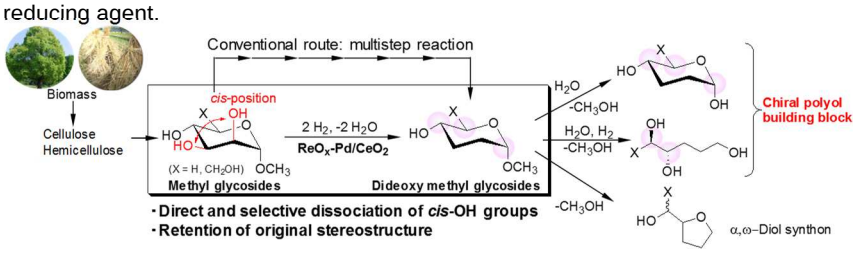
Sugar transformation: This is the first report on the single step transformation of sugars to dideoxy sugars in high stereoselectivity and regioselectivity without protecting OH groups except the OH group of the hemiacetal group using heterogeneous CeO_2-supported ReO_x and Pd (ReO_x-Pd/CeO_2) catalyst and H_2 as a reducing agent.



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Transformation of Sugars to Chiral Polyols over a Heterogeneous Catalyst