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Synthesis of Optically Active O-Protected 2,3-Dihydroxy Aldehyde

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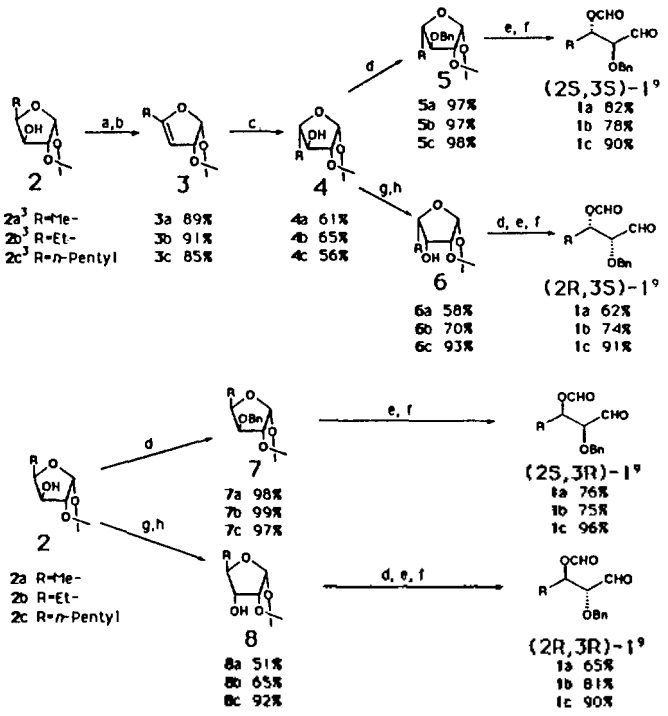
Optically active 2,3-diol units are widely distributed in the biologically active natural products such as macrolides and polyether antibiotics, etc. Recently, synthesis of syn-2,3-diol esters by asymmetric oxidation reactions of olefin esters using osmium tetroxide with a chiral ligand has been developed.[1] Also, synthesis of anti-2,3-diol esters by asymmetric aldol reaction between aldehydes and silyl enol ethers derived from α-benzyloxy thioesters with a chiral ligand was reported.[2] There still remains a need for the synthesis of optically active syn- and anti-diols on practical point of view. In connection with our current programs on the asymmetric synthesis of optically active natural products from D-glucose



(a) Tf_2O, Pyr, CH_2Cl_2, −10℃ (b) DBU, ether, rt (c) Sia_2BH, THF, 0℃→rt (d) NaH, BnCl, THF, rt (e) 2 N HCl, DME, rt (f) $NaIO_4$, MeOH, rt (g) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, −60℃→rt (h) $NaBH_4$, MeOH, −78℃.

Scheme 1

or D-xylose, we needed the appropriately protected syn- and anti-2,3-dihydroxy aldehydes **1**. Here we report a stereocontrolled synthesis of optically active four stereoisomers of 2,3-dihydroxy aldehydes by chemical modification of the α-D-glucofuranose or α-D-xylofuranose, which in turn were prepared from D-glucose or D-xylose.

Hex-3-enofuranose **3a-c** were prepared[3] by the elimination reaction of the triflates derived from C-3 hydroxyfuranoses **2a-c**.[4,5] Hydroboration of **3b** with disiamylborane followed by oxidation with H_2O_2/NaOH afforded 3-hydroxyl-β-L-threo-hexofuranose **4b**[6] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.48), $[\alpha]_D^{25}$ −25.5° (*c* 0.44, $CHCl_3$) exclusively as the only isolated produce[7] in 65% yield after column chromatographic separation. Orientation of the ethyl- and hydroxy- substituents of **4b** and excellent stereoselectivity (>99%)[7] were confirmed by the comparison of the ^{1}H- and ^{13}C-NMR spectra and capillary GLC data of **4b** and **8b** (Scheme 1).[8] Surprisingly, by capillary GLC analysis, only one isomer was detected before and after column chromatographic separation. Even if hydroboration of **3b** with BH_3·SMe_2 followed by oxidation with H_2O_2/NaOH also gave **4b** as a major product by checking GLC, hydroboration of **3b** with disiamylborane followed by oxidation afforded **4b** as the only isolated product without any impurities. Removal of the isopropylidene group in **5b** with 2 N HCl provided the hemiacetal, which was subjected to oxidative cleavage with sodium periodate to afford the (2*S*, 3*S*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ −61.8° (*c* 0.60, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*S*, 3*S*)-**1a** and (2*S*, 3*S*)-**1c**,

which is shown in Scheme 1.[8] The C-3 β-hydroxy-group in **4b** was converted to α-hydroxy-group. Swern oxidation of **4b** followed by reduction with $NaBH_4$ in MeOH at −78℃ afforded **6b**[6] as the only isolated product by checking GLC data of **6b** and **4b**. The compound **6b** was converted to the (2*R*, 3*S*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ +46.3° (*c* 1.0, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*R*, 3*S*)-**1a** and (2*R*, 3*S*)-**1c**, which is shown in Scheme 1.[8]

Alternatively, (2*S*, 3*R*)- and (2*R*, 3*R*)-2-benzyloxy-3-formyloxy-1-alkanals were easily prepared from **2**. Benzylation of **2b**[6] gave the benzyloxy compounds **7b**, which was converted to the (2*S*, 3*R*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**,[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ −47.0° (*c* 0.2, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*S*, 3*R*)-**1a** and (2*S*, 3*R*)-**1c**, which is shown in Scheme 1.[8] On the other hands, Swern oxidation of **2b** followed by reduction with $NaBH_4$ in MeOH at −78℃ afforded **8b**.[6] The compound **8b** was converted to the (2*R*, 3*R*)-2-benzyloxy-3-formyloxy-1-pentanal **1b**[9] (TLC : SiO_2, EtOAc/Hexanes = 1 : 1, R_f = 0.62), $[\alpha]_D^{25}$ +51.3° (*c* 1.97, $CHCl_3$) (Scheme 1). The reaction sequence was also applied to prepare (2*R*, 3*R*)-**1a** and (2*R*, 3*R*)-**1c**, which is shown in Scheme 1.[8]

We have used optically active *O*-protected 2,3-dihydroxy aldehydes prepared by this methodology in the enantioselective syntheses of L-factor and muricatacin.[10]

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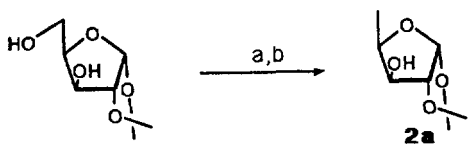
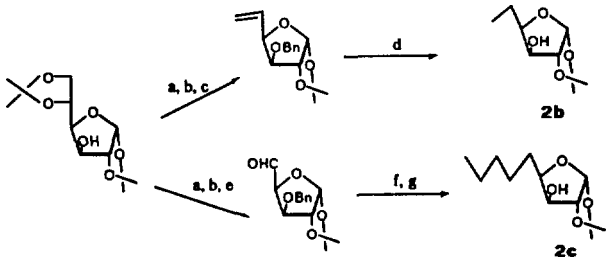
4. The compound **2a** was prepared from 1,2-*O*-isopropylidene-D-xylofuranose in two steps; (a) *p*-TsCl, pyridine, $CHCl_3$, 0℃, 12 h (79%); (b) $LiAlH_4$, THF, reflux, 12 h (96%).



5. The compounds **2b** and **2c** were prepared conventionally from diacetone-D-glucose by the following reaction sequence (a) NaH, $PhCH_2Cl$, THF, rt, 24 h (98%); (b) 50% HOAc, rt, 24 h (96%); (c) *N,N*-dimethylformamide dimethylacetal, rt, 1 h and then Ac_2O, 160℃, 3 h (71%); (d) H_2, EtOAc, Pd/C (97%); (e) $NaIO_4$, CH_2Cl_2, rt, 1 h (99%); (f) $(C_6H_5)_3P{=}CHCH_2CH_2CH_3$; (g) H_2, Pd/C, EtOAc, rt, atmospheric pressure, 24 h (88%).



6. $[\alpha]_D$ values at 25℃ (concentration in $CHCl_3$).

2a:	−18.4°(2.93)	**4a**:	−12.7°(3.0)	**6a**:	+14.2°(2.1)	**8a**: +41.0°(1.0)
2b:	−8.0°(2.0)	**4b**:	−25.5°(0.44)	**6a**:	+54.2°(0.28)	**8b**: +61.7°(1.45)
2c:	−18.0°(1.0)	**4c**:	−16.7°(1.73)	**6c**:	−61.1°(0.10)	**8c**: −95.3°(0.15)

7. Capillary GC analyses were performed for **2a-c**, **4a-c**, **6a-c**, **8a-c** using Hewlett-Packard 5880 GC system (column: Supelcowax 10, 0.25 mm×30 m, oven temp: **a**: 140℃, **b-c**: 120℃→200℃, carrier gas: N_2, 1.0 ml/min, injection temp: 250℃). The values of the retention time for each compounds were as follows: **2a**: 19.36 min, **2b**: 16.30 min, **2c**: 23.21 min, **4a**: 27.51 min, **4b**: 18.49 min, **4c**: 25.87 min, **6a**: 7.85 min, **6b**: 9.58 min, **6c**: 16.64 min, **8a**: 6.72 min, **8b**: 8.81 min, **8c**: 15.57 min.
8. All new compounds gave spectral data (IR, ^1H and ^{13}C-NMR) in accord with the assigned structure.
9. $[\alpha]_D$ values at 25℃ (concentration in $CHCl_3$).

	(2*S*, 3*S*)-1	(2*R*, 3*R*)-1	(2*R*, 3*S*)-1	(2*R*, 3*S*)-1
1a	−58.0°	+50.3°	+24.6°	−28.9°
	(0.90)	(0.3)	(0.56)	(0.98)
1b	−61.8°	+51.3°	+46.3°	−47.0°
	(0.60)	(1.97)	(1.0)	(0.21)
1c	−44.1°	+43.1°	−25.9°	+15.8°
	(0.50)	(1.50)	(1.42)	(0.50)

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Atomic Emission Detector for Gas Chromatography using Cylindrical Microwave Cavity

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The microwave induced plasma (MIP) has been increasingly applied as an excitation source for the emission detector of gas chromatography (GC).[1-5] The MIP detector is known to have high sensitivity and element selectivity, be-