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Note

Regio- and stereoselective cyclizations of dianhydro sugar alcohols catalyzed by a chiral (salen)Co^{III} complex

Toshifumi Satoh,[a,b] Tomoko Imai,[a] Satoshi Umeda,[c] Katsuyuki Tsuda,[c] Hisaho Hashimoto[d] and Toyoji Kakuchi[a,*]

[a]*Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[b]*Division of Innovative Research, Creative Research Initiative 'Sousei' (CRIS), Hokkaido University, Sapporo 001-0021, Japan*
[c]*Department of Materials Chemistry, Asahikawa National College of Technology, Asahikawa 071-8142, Japan*
[d]*Department of Science and Engineering for Materials, Tomakomai National College of Technology, Tomakomai 059-1275, Japan*

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Abstract—The (salen)Co^{III}OAc ((*R*,*R*)-**1** and (*S*,*S*)-**1**) catalyzed cyclizations of the chiral dianhydro sugars, 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**2**), 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**3**), 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**4**), and 1,2:4,5-dianhydro-3-*O*-methyl-L-arabinitol (**5**), is a facile method for the synthesis of anhydroalditol alcohols. Cyclization of **2** using (*R*,*R*)-**1** and (*S*,*S*)-**1** proceeded diastereoselectively to form 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol (**6**) and 2,5-anhydro-3,4-di-*O*-methyl-L-iditol (**7**), respectively. The cyclization of **3** and **5** is a novel method for obtaining 1,6-anhydro-3,4-di-*O*-methyl-D-mannitol (**11**) and a stereoselective route to 1,5-anhydro-3-*O*-methyl-L-arabinitol (**13**). It is proposed that the reaction occurs via *endo*-selective cyclization of an epoxy alcohol produced by the *endo*-selective ring-opening of one of the two epoxide moieties in the starting material.

Keywords: Diastereoselective cyclization; Dianhydro sugars; *endo*-Selective cyclization; *endo*-Selective ring-opening; 1,2:5,6-Dianhydrohexitol; 1,2:4,5-Dianhydropentitol

Various anhydroalditol alcohols have been prepared due not only to interest in their chemical and biochemical properties, but also due to their use as chiral building blocks for the synthesis of optically pure organic compounds.[1–8] In particular, regio- and stereoselective cyclizations of dianhydro sugars, such as 1,2:5,6-dianhydrohexitols and 1,2:4,5-dianhydropentitols, are an interesting approach for the stereocontrolled synthesis of carbohydrate derivatives.[9–16] For example, Kuszmann reported that the regio- and stereoselective cyclizations of 3,4-di-*O*-alkyl-1,2:5,6-dianhydro-D-mannitol and 3,4-di-*O*-alkyl-1,2:5,6-dianhydro-L-iditol with hydrogen bromide produced the corresponding 2,5-anhydro-6-bromo-6-deoxy-D-glucitol and 2,5-anhydro-1-bromo-1-deoxy-D-glucitol, respectively.[9] In addition, we reported that the asymmetric cyclization of *meso*-1,2:5,6-dianhydrohexitols and *meso*-1,2:4,5-dianhydropentitols using chiral (salen)Co^{III}Ac ((*R*,*R*)-**1** and (*S*,*S*)-**1**) led to chiral anhydroalditol alcohols in extremely high enantiomeric excesses.[14] These reactions arise from the enantioselective hydrolysis of one of the epoxides, followed by cyclization of the resulting diol onto the other epoxide. We were interested in further studying the cyclization of asymmetric dianhydro sugars using (*R*,*R*)-**1** and (*S*,*S*)-**1**. We report here, the diastereoselective cyclizations of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**2**) and the regio- and stereoselective cyclization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**3**), 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**4**), and 1,2:4,5-dianhydro-3-*O*-methyl-L-arabinitol (**5**), using (*R*,*R*)-**1** and (*S*,*S*)-**1** (Fig. 1).

* Corresponding author. Tel./fax: +81 11 706 6602; e-mail: kakuchi@poly-mc.eng.hokudai.ac.jp

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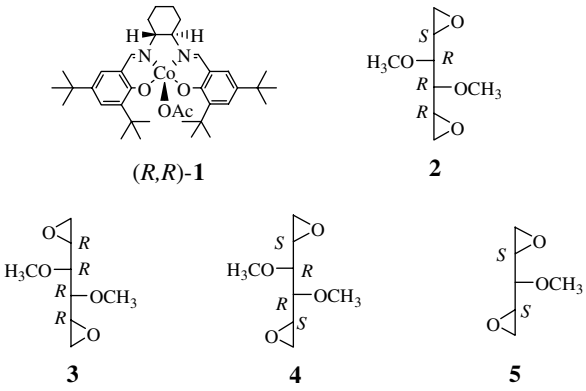
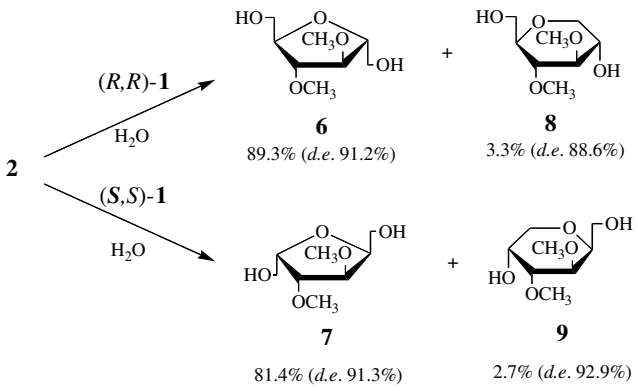


Figure 1. Structures for **1**–**5**.



Scheme 1.

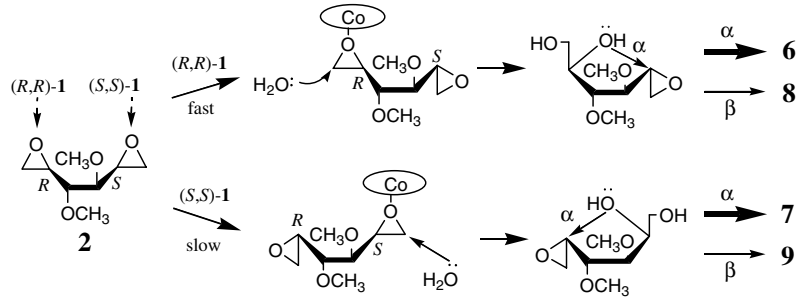
The dianhydro sugar with the (2*S*,5*R*)-configuration, **2**, possesses two epoxy groups whose reactivities are non-equivalent. The cyclization of **2** in the presence of (salen)-Co^{III}Ac **1** (0.5 mol %) was carried out with 1.1 equiv of water at room temperature. The color of the reaction mixture changed from dark brown to light brown as the reaction progressed. The reaction using (*R*,*R*)-**1** was complete in about 3 h, while that using (*S*,*S*)-**1** needed about 51 h for completion, thus showing that the cyclization of **2** with (*R*,*R*)-**1** is more efficient than that with (*S*,*S*)-**1**. The reaction results are summarized in Table 1 and compared with those of the cyclizations using HCl, KOH, and the reaction without a catalyst. The cyclizations of **2** under acidic and basic conditions gave the two five-membered ring compounds, 2,5-anhydro-3,4-di-*O*-methyl-D-mannitol (**6**) and 2,5-anhydro-3,4-di-*O*-methyl-L-iditol (**7**), and the two six-membered ring compounds, 1,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**8**) and 2,6-anhydro-3,4-di-*O*-methyl-D-glucitol (**9**), although the diastereoselectivities of these transformations were low. On the contrary, the cyclizations using **1** as a catalyst proceeded diastereoselectively to produce **6** in 89.3% (de 91.2%) yield for (*R*,*R*)-**1** and **7** in 81.4% (de 91.3%) yield for (*S*,*S*)-**1**. Two six-membered ring compounds **8** and **9** were also produced in 3.3% (de 88.6%) and 2.7% (de 92.9%) yields using (*R*,*R*)-**1** and (*S*,*S*)-**1**, respectively (Scheme 1). The diastereomeric excesses for the formation of the five-membered rings were over 90%. The proposed mechanism for the cyclization of **2** is illustrated in Scheme 2. Using (*R*,*R*)-**1**, *endo*-selective ring-opening of one of the epoxide rings is followed by cyclization to form the five-membered cyclic compound **6** as the major product. In contrast, when (*S*,*S*)-**1** is used, slow ring-opening of the other epoxide moiety proceeds, followed by *exo*-cyclization leading to the diastereomeric five-membered ring product, **7**.

Table 1. Cyclization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-glucitol (**2**) using chiral (salen)Co^{III}OAc (**1**) and other conditions

Catalyst	Time (h)	Temperature (°C)	Yield[b] (%)			
			6	**7**	**8**	**9**
(*R*,*R*)-**1**[a]	3	rt	89.3	4.1	3.3	0.2
(*S*,*S*)-**1**[a]	51	rt	3.7	81.4	0.1	2.7
HCl[a]	24	rt	37.0	35.2	10.3	9.8
KOH[a]	24	60	47.3	35.9	8.5	6.6
None (H_2O)	7	100	46.5	17.9	21.5	8.3

[a] [**2**]/[catalyst] = 200.
[b] Estimated by ^{13}C NMR using the inverse gated spin decoupling technique.

The C_2 symmetric dianhydro sugars with the (2*R*,5*R*)- and (2*S*,5*S*)-configurations (**3** and **4**, respectively) have two epoxy groups of the same reactivity. Table 2 summarizes the cyclization results of **3** and **4** using (*R*,*R*)-**1** and (*S*,*S*)-**1**. The cyclization of **3** with (*R*,*R*)-**1** proceeded rapidly at room temperature and produced 2,5-anhydro-3,4-di-*O*-methyl-D-glucitol (**10**), 1,6-anhydro-3,4-di-*O*-methyl-D-mannitol (**11**), and 1,6:2,5-dianhydro-3,4-di-



Scheme 2.

Table 2. Cyclization of 1,2:5,6-dianhydro-3,4-di-*O*-methyl-D-mannitol (**3**) and 1,2:5,6-dianhydro-3,4-di-*O*-methyl-L-iditol (**4**) using chiral (salen)Co^{III}OAc (**1**)[a]

Substrate	Catalyst	Time (h)	Yield[c] (%)		
			10	**11**	**12**
3	(*R*,*R*)-**1**	3	57.2	27.9	5.9
	(*R*,*R*)-**1**[b]	3	30.4	35.0	6.8
	(*S*,*S*)-**1**	6	0	0	0
4	(*R*,*R*)-**1**	6	0	0	0
	(*S*,*S*)-**1**	48	49.1	0	0

[a] [Substrate]/[catalyst] = 200, temperature—rt.
[b] [**3**]/[catalyst] = 0.5.
[c] Estimated by ^{13}C NMR using the inverse gated spin decoupling technique.

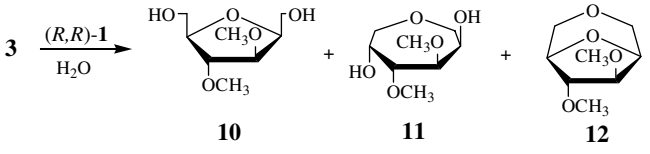
O-methyl-D-glucitol (**12**) in 57.2%, 27.9%, and 5.9% yields, respectively, as shown in Table 2 and Scheme 3. On the contrary, when (*S*,*S*)-**1** was used, no product was obtained and unreacted **3** was recovered. The proposed mechanism for the formation of the products is shown in Scheme 4. First, the dianhydro sugar alcohol **3** is coordinated with (*R*,*R*)-**1** to allow the *endo*-cleavage of the first epoxy group by water. During the next intramolecular cyclization, 5-*exo*-cyclization of the secondary hydroxyl group as predicted by Baldwin's rules[17] afforded **10**. When the second epoxy group is also coordinated with (*R*,*R*)-**1**, intramolecular cyclization leads to 7-*endo*-cyclization, as was also observed using Jacobsen's catalyst,[18] to produce the seven-membered compound **11**. It is noteworthy that the seven-membered ring product **11** was formed by the 7-*endo* cyclization of the initially formed epoxy alcohol, meaning that its formation ignored the inherent stereoelectronic preference for the intramolecular *exo*-attack during the cyclization of **3**.[17] The mechanism for the formation of **11** was supported by the following results: the increase in the molar fraction of (*R*,*R*)-**1** in the reaction system led to increasing yields of **11**. This is the first synthesis of a 3,4-*O*-disubstituted 1,6-anhydro-D-mannitol derivative.

The cyclization of **4** with **1** exhibited a different reactivity compared to that of **3**. When (*R*,*R*)-**1** was used, no reaction was observed, while the cyclization using (*S*,*S*)-**1** afforded only the five-membered ring compound **10** in 49% yield. The formation of six- and seven-membered ring analogs, or bicyclic compounds was not observed.

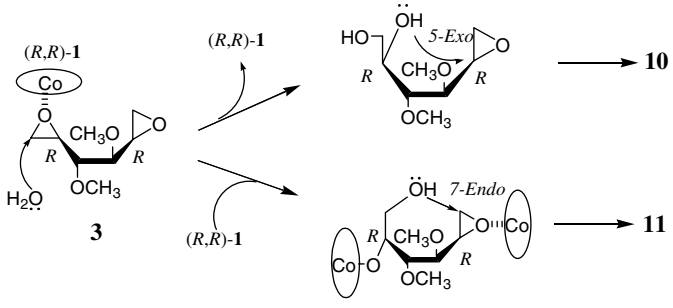
These results for the cyclizations of dianhydro sugars **2**–**4** indicate that (*R*,*R*)-**1** and (*S*,*S*)-**1** selectively coordinate to the *R*- and *S*-epoxy groups in the dianhydro sugar alcohol, respectively, leading to a stereoselective ring-opening reaction. An almost complete reaction was obtained for the cyclization of **3** with (*R*,*R*)-**1** in 3 h, while the reaction of **4** with (*S*,*S*)-**1** yielded the cyclic compounds at nearly half conversion in 48 h. Similar results were also observed for the cyclization of **2**. These phenomena can be explained by the difference in the coordinating power between the catalyst **1** and the epoxy group,[19–21] which arises from the configuration of the epoxy group and the neighboring methoxy group in the dianhydro sugars, that is, the *S*-epoxy group is in a *syn*-configuration with the neighboring methoxy group while the *R*-epoxy group is *anti*. The coordinating power between the *R*-epoxy group and (*R*,*R*)-**1**, therefore, is stronger than that between the *S*-epoxy group and (*S*,*S*)-**1** for the dianhydro sugar alcohols **2**–**4**.

Dianhydro sugar **5** has two *S*-epoxy groups, but their surroundings are nonequivalent; in one the methoxy group is *syn* while in the other this group is *anti*. As was seen for the cyclization of **2**–**4**, the reaction of **5** with (*S*,*S*)-**1** proceeded smoothly to afford 1,5-anhydro-3-*O*-methyl-L-arabinitol (**13**) in 85.0% yield, while no reaction was observed with (*R*,*R*)-**1** (Scheme 5). Compound **13** was formed through an extremely high regio- and stereoselective process, that is, the *endo*-selective ring-opening of an epoxy group in **5** followed by 6-*endo*-cyclization, as in the formation of **11** from **3**.

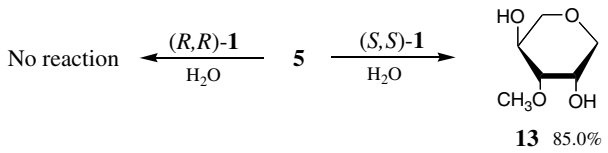
In this study, the regioselective cyclization of dianhydro-alditol derivatives was achieved using chiral (salen)Co^{III} catalysts. These reactions involve the stereoselective coordination of the catalyst with the substrate leading to the ring-opening of one epoxy group by the



Scheme 3.



Scheme 4.



Scheme 5.

addition of water followed by regioselective cyclization via ring-opening of the remaining epoxy group. The difference in the coordinating power between the catalyst and the epoxy group arises from the configuration of the epoxy group and the neighboring methoxy group. The coordinating power with the catalyst was shown to be stronger when the epoxy group is *anti* to this substituent as opposed to *syn*. As a result, these cyclizations formed specific anhydroalditol alcohols in a highly stereoselective manner.

1. Experimental

1.1. General methods

The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400 II spectrometer. All signals were expressed as ppm downfield from tetramethylsilane used as the internal standard (δ value in $CDCl_3$). Diastereomeric excess (de) values were estimated by ^{13}C NMR using the inverse gated spin decoupling technique with a 7.0 s delay and 6000 scans at 25 °C (45° pulse angle). Optical rotations were measured using a JASCO DIP 1000 digital polarimeter with a sodium lamp. D-Arabinitol was prepared by the reduction of D-arabinose.[22] The catalysts (*R*,*R*)-**1** and (*S*,*S*)-**1** were prepared by reported procedures.[23] For the preparation of **2**, **3**, and **4**, the Kuszmann method was used.[24] These dianhydro sugars were distilled over CaH_2 under vacuum before the reactions. Column chromatography was performed using silica gel 60 (particle size 0.063–0.200 mm, Merck). Thin-layer chromatography was performed using silica gel 60 F_{254} (0.25 mm thick, Merck).

1.2. General procedure for the cyclization of dianhydro sugar alcohols

All reactions were carried out under ambient atmosphere. A typical procedure is as follows: Water (57 μL, 3.17 mmol) was added to **2** (0.50 g, 2.87 mmol) and (*R*,*R*)-**1** (9.2 mg, 1.39×10^{-2} mmol), and the mixture was stirred for 3 h while occasionally checking the progress of the reaction by thin-layer chromatography. After the reaction was complete, the mixture was diluted with water, filtered through a membrane (nitrocellulose, 1.0 μm), and the filtrate concentrated. To estimate the conversion, the residue was analyzed by ^{13}C NMR spectroscopy using the inverse gated spin decoupling technique. The residue was purified by column chromatography.

1.3. 1,2:4,5-Dianhydro-3-*O*-methyl-L-arabinitol (5)

Compound **5** was prepared from D-arabinitol as previously described (see Supplementary data).[13] Bp 73 °C (22 mmHg); $[\alpha]_D^{23}$ −10.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.66 (dd, 1H, $J = 4.9$, 2.9 Hz, CH_2), 2.76 (dd, 1H, $J = 5.0$, 2.7 Hz, CH_2), 2.79–2.87 (m, 3H), 3.05 (ddd, 1H, $J = 5.6$, 2.9, 2.7 Hz, CH), 3.12 (ddd, 1H, $J = 6.6$, 2.9, 2.7 Hz, CH), 3.50 (s, 3H, –OCH_3); ^{13}C NMR ($CDCl_3$): δ 42.92 (CH_2), 45.26 (CH_2), 50.69 (CH), 52.35 (CH_2), 58.29 (–OCH_3), 81.82 (CH). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 54.70; H, 7.59.

1.4. 2,5-Anhydro-3,4-di-*O*-methyl-D-mannitol (6) and 1,5-anhydro-3,4-di-*O*-methyl-D-glucitol (8)

Compounds **6** and **8** were obtained by the reaction of **2** with water and (*R*,*R*)-**1** for 3 h at rt. After removing the catalyst, the residue was purified by column chromatography using EtOAc/CH_3OH (5/1) as the eluant. Evaporation of the fractions having R_f values of 0.34 and 0.45 gave **6** (colorless liquid, 89.3% yield (de 91.2%)), and **8** (colorless liquid, 3.3% yield (de 88.6%)), respectively. Compound **6**: ^{1}H NMR ($CDCl_3$): δ 4.15–4.01 (m, 2H), 3.80–3.62 (m, 6H), 3.40 (s, 6H, –OCH_3), 2.95–2.73 (br s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ 85.80 (CH), 83.21 (CH), 62.70 (–CH_2OH), 57.59 (–OCH_3). Compound **8**: ^{1}H NMR ($CDCl_3$): δ 3.94 (dd, 1H $J = 11.2$, 5.6 Hz), 3.74–3.63 (m, 5H), 3.50 (s, 3H, –OCH_3), 3.46 (s, 3H, –OCH_3), 3.24–3.12 (m, 1H), 3.04–3.01 (m, 1H), 2.85 (br s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ 88.22 (CH), 79.89 (CH), 79.50 (CH), 69.65 (CH), 69.27 (–CH_2OH), 61.68 (–CH_2OH), 60.68 (–OCH_3), 60.16 (–OCH_3).

1.5. 2,5-Anhydro-3,4-di-*O*-methyl-L-iditol (7) and 2,6-anhydro-3,4-di-*O*-methyl-D-glucitol (9)

Compounds **7** and **9** were obtained by the reaction of **2** with water and (*S*,*S*)-**1** for 51 h at rt. The products were purified by column chromatography using EtOAc/CH_3OH (5/1) as the eluant. Evaporation of fractions having R_f values of 0.35 and 0.45 gave **7** (colorless liquid, 81.4% yield (de 91.3%)) and **9** (colorless liquid, 2.7% yield (de 92.9%)), respectively. Compound **7**: ^{1}H NMR ($CDCl_3$): δ 4.30–4.20 (m, 2H), 3.96 (d, 2H), 3.90–3.75 (m, 4H), 3.45 (s, 6H, –OCH_3), 2.48–2.30 (br s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ 84.91 (CH), 79.44 (CH), 61.62 (–CH_2OH), 58.06 (–OCH_3). Compound **9**: ^{1}H NMR ($CDCl_3$): δ 4.09–4.03 (m, 1H), 3.84–3.60 (m, 5H), 3.54 (s, 6H, –OCH_3), 3.24–3.10 (m, 2H), 3.06 (br s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ 76.05 (CH), 75.91 (CH), 74.57 (CH), 66.45 (CH), 64.45 (–CH_2OH), 61.92 (–CH_2OH), 58.52 (–OCH_3), 58.46 (–OCH_3).

1.6. 2,5-Anhydro-3,4-di-*O*-methyl-D-glucitol (10), 1,6-anhydro-3,4-di-*O*-methyl-D-mannitol (11) and 1,6:2,5-dianhydro-3,4-di-*O*-methyl-D-glucitol (12)

Compounds **10**–**12** were obtained by the hydration of **3** with (*R*,*R*)-**1** after 3 h at rt. After removing the catalyst, the products were purified by column chromatography using EtOAc/acetone (1/1) as the eluant. Evaporation of the fractions having R_f values of 0.37, 0.25, and 0.66 gave **10** (colorless liquid, 57.2% yield), **11** (colorless liquid, 27.9% yield), and **12** (colorless liquid, 5.9% yield), respectively. Compound **10**: the ^{1}H NMR and ^{13}C NMR chemical shifts of **10** were as reported previously.[11] Compound **11**: ^{1}H NMR ($CDCl_3$): δ 4.20–4.05 (m, 2H, H-2,5), 3.95–3.60 (m, 6H, H-1,3,4,6), 3.52 (s, 6H, –OCH_3), 2.75–2.63 (br s, 2H, –OH); ^{13}C NMR ($CDCl_3$): δ 81.39 (C-3,4), 71.39 (C-1,6), 69.20 (C-2,5), 59.16 (–OCH_3). Anal. Calcd for $C_8H_{16}O_5$: C, 49.99; H, 8.39. Found: C, 49.69; H, 8.48. FD-MS *m*/*z* (relative intensity), 192 (M^+−100), 193 (MH^+−28.8). Compound **12**: ^{1}H NMR and ^{13}C NMR chemical shifts of **12** were the same as reported previously.[11]

1.7. 1,5-Anhydro-3-*O*-methyl-L-arabinitol (13)

Compound **13** was obtained by the reaction of **5** with water and (*S*,*S*)-**1** for 48 h at rt. After removing the catalyst, the products were purified by column chromatography using EtOAc as the eluant. Evaporation of the fractions having an R_f value of 0.25 gave **13** (colorless oil, 85.0%). $[\alpha]_D^{25}$ +77.8 (*c* 1.0, $CHCl_3$), ^{1}H NMR (D_2O): δ 4.23 (m, 1H, H-4), 3.91 (m, 3H, H-1,2,5), 3.58 (dt, 1H, H-5), 3.46 (s, 3H, –OCH_3), 3.32 (dq, 1H), 3.21 (t, 1H, H-1); ^{13}C NMR (D_2O): δ 85.01 (C-3), 72.73 (C-5), 72.09 (C-1), 68.38 (C-2), 67.26 (C-4), 58.89 (–OCH_3). Anal. Calcd for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: C, 48.39; H, 8.08.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2005.09.003.

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