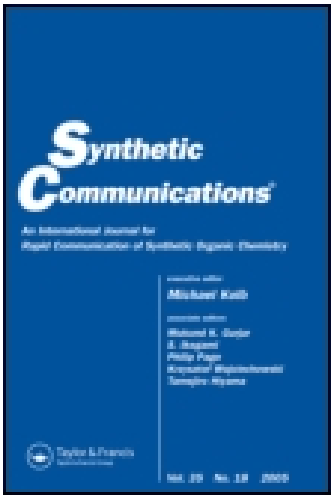


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Epoxidation of Protected (1,4,5)-Cyclohex-2-ene-triols and Their Acid Hydrolysis to Synthesize Quercitols from D-(-)-Quinic Acid

Tzenge-Lien Shih [a] & Ya-Ling Lin [a]
[a] Department of Chemistry , Tamkang University , Tamsui, Taipei County, Taiwan, Republic of China
Published online: 15 Aug 2006.

To cite this article: Tzenge-Lien Shih & Ya-Ling Lin (2005) Epoxidation of Protected (1,4,5)-Cyclohex-2-ene-triols and Their Acid Hydrolysis to Synthesize Quercitols from D-(-)-Quinic Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:13, 1809-1817, DOI: 10.1081/SCC-200063960

To link to this article: http://dx.doi.org/10.1081/SCC-200063960

Synthetic Communications®, 35: 1809–1817, 2005

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1081/SCC-200063960

Taylor & Francis
Taylor & Francis Group

Epoxidation of Protected (1,4,5)-Cyclohex-2-ene-triols and Their Acid Hydrolysis to Synthesize Quercitols from D-(−)-Quinic Acid

Tzenge-Lien Shih and Ya-Ling Lin
Department of Chemistry, Tamkang University, Tamsui, Taipei County, Taiwan, Republic of China

Abstract: Highly stereoselective epoxidations have been achieved in both cyclohexylidene acetal and butane 2,3-bisacetal (BBA) protection of (1,4,5)-cyclohex-2-ene-triols. These epoxy derivatives are all derived from D-(−)-quinic acid and can be used for the synthesis of *muco*-, (+)-*epi*-, (+)-*vibo*, (−)-*talo*, and (−)-*gala*-quercitols.

Keywords: D-(−)-Quinic acid, epoxidation, quercitol

INTRODUCTION

Quercitol has been used as a generic term for deoxyinositol or cyclohexanepentol. The quercitol's family contains 16 stereoisomers[1] that bear resemblance to the parent carbohydrates. Not only are they considered as potential inhibitors of glycosidases but they also possess other related biological activities.[2] Therefore, their syntheses have brought a great deal of attention to the synthetic community.[3] Recently, we have reported the synthesis of five quercitols, included *neo*, (−)-*epi*-, (−)-*allo*-, (−)-*talo*-, and (+)-*gala*-quercitols, from dihydroxylation of intermediates **2**, **3**, and **5**, which were all derived from D-(−)-quinic acid (Figure 1).[4] In that

Received in Japan January 11, 2005
Address correspondence to Tzenge-Lien Shih, Department of Chemistry, Tamkang University, Tamsui 25137, Taipei County, Taipei, Taiwan, Republic of China. Tel.; Fax: 886-2-86315024; E-mail: tlshih@mail.tku.edu.tw

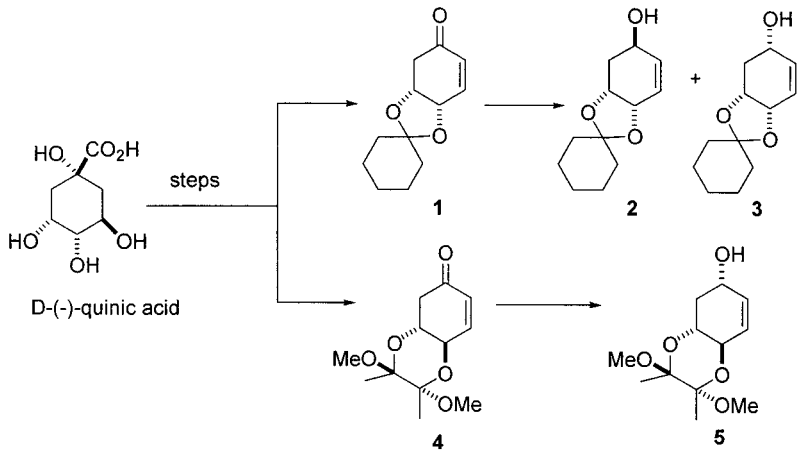
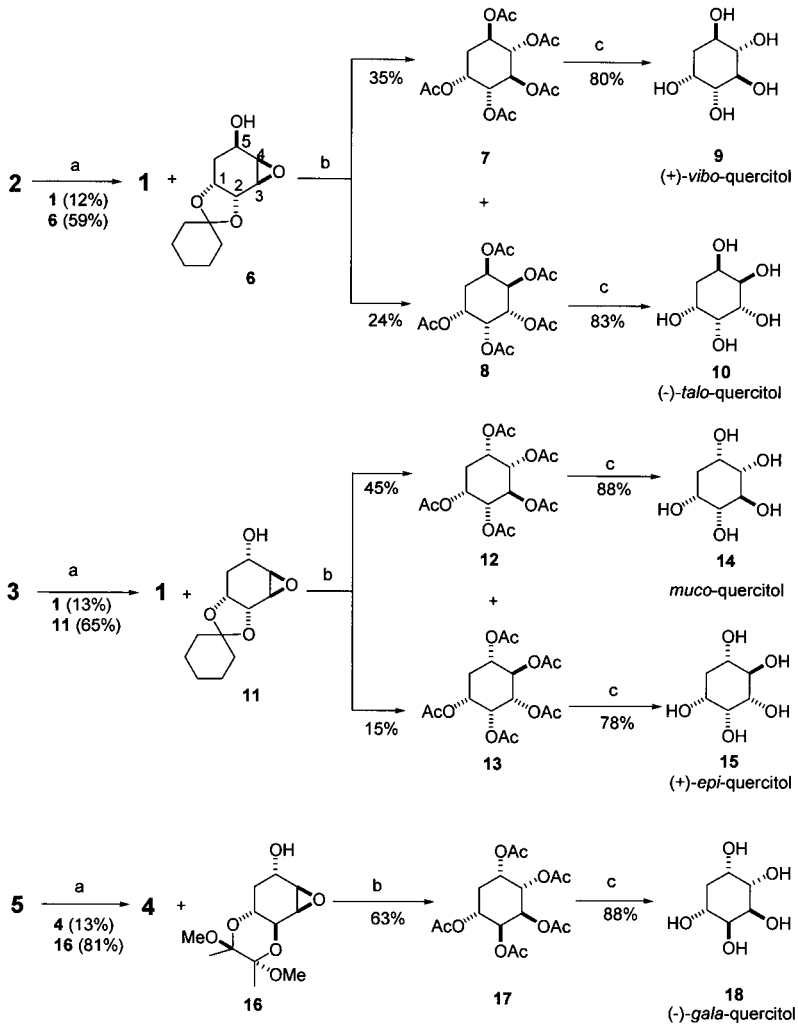


Figure 1. Compounds **2**, **3**, and **5** for epoxidation studies.

article, we had demonstrated that the stereochemistry of dihydroxylation of **2**, **3**, and **5** could be controlled by choosing appropriate protecting groups. When the isopropylidene group was used for protection racemic **2** instead of cyclohexyl acetal moiety, its epoxidation was highly stereoselective. The resulting epoxy derivative was later used for the synthesis of (±)-*vibo*- and (±)-*talo*-quercitols.[5] It prompted us that we could further investigate the epoxidation of **3** and **5** to determine how the cyclohexylidene acetal or butane 2,3-bisacetal (BBA) groups were able to control the outcomes of their stereochemistry as in compound **2**. Therefore, compounds, **2**, **3**, and **5** were subjected to oxidation with *m*CPBA (1.2 eq) to provide epoxy compounds **6** (59%), **11** (65%), and **16** (81%), respectively (Scheme 1). During this course, either enone **1** or **4** was always formed in yields of 12–13%. Compounds **6**, **11**, and **16** were hydrolyzed under Ac_2O/H_2SO_4 (cat) condition, and then deacetylated to afford the *muco*-, (+)-*epi*-, (+)-*vibo*-, (−)-*talo*-, and (−)-*gala*-quercitols (vide infra).

RESULTS AND DISCUSSION

When **2** was oxidized with *m*CPBA (1.2 eq), the required epoxy **6** along with **1** were received in yields of 59% and 12% respectively. (A higher yield (94%) was obtained in isopropylidene protection of racemic **2** instead of cyclohexyl acetal group with sonication condition. See Ref. 5.) Effort had been made to isolate the other stereoisomer of **6** but failed. We suspected that enone **1** might be derived from this unstable minor stereoisomer or **6** after elimination.[6] This kind of phenomen also occurred for compounds **3** and **5** in their epoxidation (vide infra). Thus, we could not rule out the possibility of



Scheme 1. Reagents and conditions: (a) *m*CPBA (1.2 eq), $NaHPO_4 \cdot 12H_2O$, CH_2Cl_2; (b) Ac_2O, H_2SO_4 (cat), reflux; (c) 7N NH_3/MeOH.

the formation of the other diastereoisomers during the epoxidation of compounds **2**, **3**, and **5**, respectively. The stereochemistry of epoxy **6** was determined by no NOE (Nuclear Overhausier Enhancement) between H_2 and H_3. The acid hydrolysis of **6** with a catalytic amount of concentrated sulfuric acid in acetic anhydride under reflux condition[5] afforded the (+)-*vibo*-quercitol pentaacetate (**7**)[1,7] and (−)-*talo*-quercitol pentaacetate (**8**)[1,8] in a ratio of 1.46:1. It was not surprising that the hydrolysis favored attacking at the less-hindered site at C4 over C3. Deacetylation of **7** and **8**

provided the (+)-*vibo*-quercitol (**9**)[1,5,9] and (−)-*talo*-quercitol (**10**),[1,5,8,10] respectively. However, at least in our present results, the ratio between **7** and **8** were in contrast to those of Balci's method.[5] The ratio of (±)-*vibo*-quercitol pentaacetate versus (±)-*talo*-quercitol pentaacetate from their preparation was 1:4, although *O*-isopropylidene group was employed instead of cyclohexylidene acetal group in **6** before acid hydrolysis.

When compound **3** underwent epoxidation, epoxy **11** along with enone **1** were isolated in yields of 65% and 13%, respectively. The stereochemistry of **11** could be unambiguously determined by its NOESY spectrum because of no observance of NOE between H_2 and H_3. The highly stereoselective epoxidation of **2** was claimed to be hydrogen-bond-directing effect.[5] However, the epoxidation of **3** occurred at the opposite face to the C5-OH and cyclohexylidene acetal groups. We suggested that the reaction of **5** might not involve a directing effect from the hydrogen bond. Meanwhile, out result strongly supported the theory that the steric effect arising from cyclohexylidene acetal group controlled the outcome of stereochemistry. Whereas epoxy **11** was treated with the same manner as previous,[5] pentaacetates **12** and **13** were isolated in yields of 45% and 15%, respectively. (For physical data for *muco*-quercitol pentaacetate and (+)-*epi*-quercitol pentaacetate, See Ref. 1.) Subsequently, compounds **12** and **13** were deacetylated by 7N NH_3 in methanol to provide the *muco*-quercitol (**14**)[11] and (+)-*epi*-quercitol (**15**),[1,12] respectively. Their spectroscopic data were all in accordance with the reported values.

The oxidation of **5** gave epoxy **16** as well as enone **4** in yields of 81% and 13%, respectively. The indicated stereochemistry of **16** was based on the observance of NOE between H_2 and H_3, and also H_3/H_4 and H_{6a}. The highly regioselective opening of oxirane ring of **16** occurred exclusively at C4, resulting in **17**[1,13] as the role product in 63% yield. This result was contrast to the cases in **6** and **11** in which low regioselectivity was obtained. The subsequent deacetylation of **17** gave the (−)-*gala*-quercitol (**18**).[10b,12b,13,14] The overall results were summarized in Table 1.

CONCLUSION

In conclusion, we have successfully synthesized five quercitols in eight steps each from acid hydrolysis of epoxy **6**, **11**, and **16**, which were all derived from the highly stereoselective oxidation, of **2**, **3**, and **5**, respectively. It is worth noting that the epoxidation of **2** and **3** was highly stereoselective to the *anti* sense of the cyclohexylidene acetal group but not related to the stereochemistry of C5-OH. Therefore, the steric effect arising from the cyclohexylidene acetal group did play an important role to the results. Despite **5** being dihydroxylated to give moderate stereoselective products,[4] to our surprise it was oxidized in high stereoselectivity to give **16** in which oxirane was the

Table 1. Physical data for quercitols and their corresponding pentaacetate derivatives

Compound	Pentaacetate	$[\alpha]_D$, Mp (°C) (literature)	Quercitol	$[\alpha]_D$, Mp (°C) (literature)
6	**7**	+20 (−22)[a]	**9**	+47.6, 183–185 (−50, 181)[c]
	8	−25.4, 184–187 (+28, 183)[b]	**10**	−65, 238–248 (+61, 248)[d]
11	**12**	172–174 (168)[e]	**14**	229–232 (230–232)[g]
	13	+16.2 (−14.5)[f]	**15**	+5, 188–190 (+7, 197–199)[h]
16	**17**	−22.4 (−24, 117)[e]	**18**	−53, 249–256 (−48, 258)[e]

[a]Ref. 1 for (−)-*vibo*-quercitol pentaacetate.
[b]Ref. 1 for (+)-*talo*-quercitol pentaacetate.
[c]Ref. 1 for (−)-*vibo*-quercitol.
[d]Ref. 1 for (+)-*talo*-quercitol.
[e]Ref. 1.
[f]Ref. 4 for (−)-*epi*-quercitol pentaacetate.
[g]Ref. 11a.
[h]Ref. 15b.

same face with its C2 stereochemistry. The acid-promoted ring opening of oxirane **6** and **11** had low regioselectivity that favored C4 over C3 and resulted in **7** and **12** as the major products, respectively. On the contrary, the ring opening attacked exclusively at C4 over C3 in **16** to give pentaacetate **17** as the only isolated molecule. Among these synthesized quercitols, to the best of our knowledge, the (+)-*vibo*- and (−)-*talo*-quercitols have never been prepared until now.

EXPERIMENTAL

General Procedure for Epoxidation

The reaction was conducted in 0.2 M of solution. To a stirred solution of **2**, for example, in CH_2Cl_2 was added 55% *m*CPBA (1.2 eq) and $Na_2HPO_4 \cdot 12H_2O$ (1.2 eq) at ambient temperature. The reaction was monitored by TLC until completion. The resulting mixture was diluted with CH_2Cl_2 and washed with $NaHCO_3$ (sat.). The organic layer was dried ($MgSO_4$), concentrated, and purified by flash column chromatography.

(*1R*,2*R*,3*R*,4*S*,5*R*)-3,4-Epoxy-5-hydroxy-1,2-*O*-cyclohexylidene-l,2-dihydroxy-cyclohexane (6): ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.20–4.40 (m, 3H), 3.37 (d, $J = 4.5$ Hz, 1H), 3.20 (dd, $J = 4.5$, 1.2 Hz, 1H), 2.17 (ddd, $J = 14.5$, 6.3, 3.0 Hz, 1H), 1.41–1.72 (m, 9H), 1.39 (br, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 109.8, 73.1, 69.6, 64.1, 55.9, 55.4, 37.4, 34.8, 27.2, 25.0, 24.0, 23.7. Mp 78–79°C.

(+)-*Vibo*-quercitol pentaacetate [(+)-*penta*-*O*-acetyl-1-deoxy-*myo*-inositol] (7): $[\alpha]_D^{27} + 20$ (*c* 0.2, $CHCl_3$) [lit.[1] −22 for (−)-*vibo*-quercitol pentaacetate]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.39–5.49 (m, 2H), 5.20–5.31 (m, 1H) 5.16 (t, $J = 9.7$ Hz, 1H), 4.95 (dd, $J = 10.4$, 3.1 Hz, 1H), 2.29 (dt, $J = 14.3$, 4.1 Hz, 1H), 2.15 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H), 1.99 (s, 3H), 1.74 (ddd, $J = 14.3$, 11.6, 2.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 169.9 (×2), 169.8, 169.7, 73.2, 71.4, 69.6, 68.4, 66.8, 30.7, 20.9, 20.8, 20.6.

(−)-*Talo*-quercitol pentaacetate [(−)-*penta*-*O*-acetyl-l-deoxy-l-*neo*-inositol] (8): $[\alpha]_D^{24} - 25.4$ (*c* 0.3, $CHCl_3$) (lit.[1] + 28, lit.[8] + 24 for (+)-*talo*-quercitol pentaacetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (br s, 1H), 5.52 (dd, $J = 6.3$, 3.3 Hz, 1H), 5.31 (dd, $J = 10.6$, 2.8 Hz, 1H), 5.23 (ddd, $J = 11.3$, 5.1, 2.8 Hz, 1H), 5.20 (dd, $J = 10.6$, 3.3 Hz, 1H), 1.90–2.20 (m + 5 × CH_3CO, 17H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 170.1, 170.0, 169.9, 169.6, 69.6, 69.0, 67.7, 66.8, 66.1, 28.9, 20.9, 20.7, 20.6, 20.5. Mp 184–187°C. (lit.[1] 183°C, lit.[8] 172–178°C, lit.[10c] 182–183°C). HRMS (FAB) calcd. for $C_{13}H_{26}O_{10}$ ($M^+ + H$) 375.1291. Found 375.1281.

(+)-*Vibo*-quercitol [(+)-1-deoxy-*myo*-inositol] (9): $[\alpha]_D^{26} + 47.6$ (*c* 0.2, H_2O) (lit.[1] −50 for (−)-*vibo*-quercitol). ^{1}H NMR (300 MHz, D_2O): δ 3.96 (m, 1H), 3.67 (ddd, $J = 14.0$, 9.3, 4.7 Hz, 1H), 3.48 (dd, $J = 18.6$, 9.0 Hz, 1H), 3.39 (dd, $J = 9.8$, 3.0 Hz, 1H), 3.15 (t, $J = 9.2$ Hz, 1H), 2.00 (dt, $J = 14.0$, 3.9 Hz, 1H), 1.45 (ddd, $J = 14.4$, 12.3, 2.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $D_2O + CD_3OD$): δ 78.3, 74.6, 73.6, 69.2, 36.0. Mp 183–185°C. (lit.[1] 181°C). HRMS (FAB) calcd. for $C_6H_{13}O_5$ ($M^+ + H$) 165.0763. Found 165.0754.

(−)-*Talo*-quercitol [(−)-1-deoxy-*allo*-inositol] (10): $[\alpha]_D^{24} - 65$ (*c* 0.5, H_2O) (lit.[1] + 61, lit.[10a] + 56.4, lit.[8] + 34 for (+)-*talo*-quercitol). ^{1}H NMR (300 MHz, D_2O): δ 3.82–4.05 (m, 3H), 3.52–3.57 (br. s, 2H), 1.78 (dd, $J = 10.0$, 3.2 Hz, 2H). ^{13}C NMR (75.4 MHz, $D_2O + CD_3OD$): δ 73.7, 71.4, 70.8, 68.8, 66.8, 33.2. Mp 238–248°C (lit.[1] 248°C, lit.[10c] 245–248°C). HRMS (FAB) calcd. for $C_6H_{13}O_5$ ($M^+ + H$) 165.0763. Found 165.0764.

(1*R*,2*R*,3*R*,4*R*,5*S*)-3,4-Epoxy-5-hydroxy-1,2-*O*-cyclohexylidene-1,2-dihydroxy-cyclohexane (11): ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (d, $J = 5.6$ Hz, 1H), 4.27–4.33 (m, 1H), 4.12–4.22 (m, 1H), 3.50 (d, $J = 10.9$ Hz, OH), 3.34

(d, $J = 3.3$ Hz, 1H), 3.09 (d, $J = 3.3$ Hz, 1H), 2.7 (dt, $J = 15.7$, 2.6 Hz, 1H), 1.84 (ddd, $J = 15.7$, 4.1, 1.6 Hz, 1H), 1.52–1.72 (m, 8H), 1.31–1.46 (br, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 109.7, 71.5, 70.2, 64.2, 54.0, 52.2, 37.9, 34.7, 24.9, 24.8, 24.0, 23.6.

***Muco*-quercitol pentaacetate [*penta-O*-aetyl-3-deoxy-*epi*-inositol] (12):** ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.65 (t, $J = 9.4$ Hz, 1H), 5.35 (dd, $J = 7.2$, 3.5 Hz, 2H), 4.99 (dd, $J = 9.4$, 3.5 Hz, 2H), 2.33 (dt, $J = 15.7$, 4.1 Hz, 1H), 2.10 (s, 6H), 2.04 (s, 3H), 2.02 (s, 6H), 1.89 (dt, $J = 15.7$, 3.6 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 170.0, 169.8, 169.6, 70.9, 67.6, 67.5, 28.7, 20.9, 20.7, 20.6. Mp 172–174°C. (lit.[1] 168°C).

(+)-*Epi*-quercitol pentaacetate [(−)-*penta-O*-acetyl-2-deoxy-*epi*-inositol] (13): $[\alpha]_D^{26} + 16.2$ (c 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.50–5.60 (m, 1H), 5.40 (t, $J = 10.2$ Hz, 1H), 4.85–5.10 (m, 3H), 2.20–2.30 (m, 1H), 2.18 (s, 3H), 2.14 (dd, $J = 7.7$, 6.7 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 170.1, 169.9, 169.8, 169.6, 169.5, 70.7, 69.3, 69.2, 68.7, 66.0, 29.4, 20.8, 20.7, 20.6, 20.5. HRMS (FAB) calcd. for $C_{13}H_{26}O_{10}$ ($M^+ + H$) 375.1291. Found 375.1295.

***Muco*-quercitol [3-deoxy-*epi*-inositol] (14):** ^{1}H NMR (300 MHz, D_2O): δ 3.96 (dd, $J = 6.6$, 3.2 Hz, 2H), 3.79 (t, $J = 9.3$ Hz, 1H), 3.41 (dd, $J = 9.3$, 3.2 Hz, 2H), 2.03 (dt, $J = 15.4$, 4.0 Hz, 1H), 1.64 (dt, $J = 15.4$, 3.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $D_2O + CD_3OD$): δ 74.9 (× 2), 71.5 (× 2), 71.2, 32.6. Mp 229–232°C. (lit.[10a] 230–232°C). HRMS (FAB) calcd. for $C_{13}H_{26}O_{10}$ ($M^+ + H$) 375.1291. Found 375.1295.

(+)-*Epi*-quercitol [(+)-2-deoxy-*epi*-inositol] (15): $[\delta]_D^{25}$ +5.2 (c 0.3, H_2O) (lit.[12] +7). ^{1}H NMR (300 MHz, D_2O): δ 3.88 (dd, $J = 2.9$, 1.4 Hz, 1H), 3.60–3.75 (m, 1H), 3.35–3.40 (m, 2H), 3.31 (dd, $J = 10.2$, 2.9 Hz, 1H), 1.82–1.92 (m, 1H), 1.64 (dt, $J = 11.8$, 5.9 Hz, 1H). ^{13}C NMR (75.4 MHz, $D_2O + CD_3OD$): δ 75.2, 73.8, 72.7, 70.2, 67.4, 34.8. Mp 188–190°C. (lit.[12] 197–199°C).

(1*R*,2*R*,3*S*,4*R*,5*S*)-3,4-Epoxy-5-hydroxy-1,2-[(2*S*,3*S*)-2,3-dimethoxybutane-2,3-diyldioxy]cyclohexane (16): ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.18 (ddd, $J = 10.2$, 6.5, 2.3 Hz, 1H), 3.74 (d, $J = 9.7$ Hz, 1H), 3.41 (ddd, $J = 12.5$, 9.7, 2.8 Hz, 1H), 3.30–3.47 (m, 1H), 3.32 (s, 3H), 3.26 (d, $J = 3.7$ Hz, 1H), 3.24 (s, 3H), 1.95 (ddd, $J = 12.5$, 6.5, 2.8 Hz, 1H), 1.70 (br, OH), 1.36 (dd, $J = 12.5$, 10.2 Hz, 1H), 1.33 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 100.3, 99.8, 68.7, 67.9, 66.3, 56.1 (× 2), 48.0, 47.9, 30.7, 17.6. Mp 134–135°C. LRMS (FAB) m/z 259 (M^+-H, 9%)

(−)-*Gala*-quercitol pentaacetate [(−)-*penta-O*-acetyl-2-deoxy-*allo*-inositol] (17): $[\alpha]_D^{24}$ −22.4 (c 0.6, $CHCl_3$) (lit.[1] −24). ^{1}H NMR (300 MHz, $CDCl_3$): δ

5.38 (dd, $J = 5.3$, 3.4 Hz, 1H), 5.20–5.30 (m, 3H), 5.11 (ddd, $J = 13.4$, 8.8, 4.6 Hz, 1H), 2.15–2.25 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.97–2.06 (m + 3 × CH_3CO, 10H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 169.8, 169.4 (×2), 69.8, 68.2, 67.7, 66.7, 29.1, 20.9, 20.8, 20.7.

(−)-*Gala*-quercitol [(−)-2-deoxy-*allo*-inositol] (18): $[\alpha]_D^{25}$ −53 (*c* 0.3, H_2O) (lit.[1] −48, lit.[10b,14] −50). ^1H NMR (300 MHz, D_2O): δ 3.87–3.97 (m, 2H), 3.82 (t, $J = 3.3$ Hz, 1H), 3.70 (ddd, $J = 11.2$, 9.0, 4.5 Hz, 1H), 3.58 (dd, $J = 9.0$, 3.3 Hz, 1H), 1.90 (dt, $J = 11.6$, 4.5 Hz, 1H), 1.62 (dt, $J = 11.6$, 11.2 Hz, 1H). ^{13}C NMR (75.4 MHz, $D_2O + CD_3OD$): δ 73.1, 72.9, 72.6, 68.8, 67.3, 34.4. Mp 249–256°C, (lit.[1] 258°C, lit.[10b,14] 256–257°C). HRMS (FAB) calcd. for $C_6H_{13}O_5$ ($M^+ + H$) 165.0763. Found 165.0771.

ACKNOWLEDGMENT

We gratefully acknowledge the National Science Council (NSC92-2113-M-032-004) and Tamkang University for supporting this work.

REFERENCES

1. McCasland, G. E.; Furta, S.; Johnson, L. F.; Shoolery, J. N. *J. Am. Chem. Soc.* **1961**, *83*, 2335–2343.
2. (a) Lillelund, V. H.; Jensen, H. H.; Liang, X.; Bols, M. *Chem. Rev.* **2002**, *102*, 515–554; (b) Sinnott, M. L. *Chem. Rev.* **1990**, *90*, 1171–1202.
3. Hudlicky, T.; Cebulak, M. *Cyclitols and Their Derivatives*; VCH: New York, 1993.
4. Shih, T.-L.; Lin, Y.-L.; Kuo, W.-S. *Tetrahedron* **2005**, *61*, 1919–1924.
5. Maras, A.; Secen, H.; Siitbeyaz, Y.; Balci, M. *J. Org. Chem.* **1998**, *63*, 2039–2041.
6. For a similar mechanism. See Doris, E.; Dechoux, L.; Mioskowski, C. *J. Am. Chem. Soc.* **1995**, *117*, 12700–12704.
7. For physical data for (±)-*vibo*-quercitol pentaacetate, see: (a) Salamci, E.; Secen, H.; Sütbeyaz, Y.; Balci, M. *Synth. Commun.* **1997**, *27*, 2223–2234; (b) For (−)-*vibo*-quercitol pentaacetate.
8. For physical data for (+)-*talo*-quercitol pentaacetate. See Yadav, J. S.; Maiti, A.; Sankar, A. R.; Kunwar, A. C. *J. Org. Chem.* **2001**, *66*, 8370–8378.
9. Physical data for (±)-*vibo*-quercitol: (a) Cambie, R. C.; Renner, N. D.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1990**, *43*, 1597–1602; (b) McCasland, G. E.; Horswill, E. C. *J. Am. Chem. Soc.* **1953**, *75*, 4020–4026and Ref 5. Physical data for (+)-*vibo*-quercitol; (c) Posternak, T. *Helv. Chim. Acta.* **1950**, *33*, 1594–1597; Physical data for (−)-*vibo*-quercitol; (d) Ogawa, S.; Uetsuki, S.; Tezuka, Y.; Morikawa, T.; Takahashi, A.; Sato, K. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1493–1498.
10. Physical data for (+)-*talo*-quercitol, see Ref. 1 and (a) Hyldtoft, L.; Madsen, R. J. *Am. Chem. Soc.* **2000**, *122*, 8444–8452; (b) Angelaud, R.; Babot, O.; Charvat, T.; Landais, Y. *J. Org. Chem.* **1999**, *64*, 9613–9624; (c) McCasland, G. E.; Furuta, S.; Bartuska, V. *J. Org. Chem.* **1963**, *28*, 2096–2101.

11. Angyal, S. J.; Odier, L. *Carbohydr. Res.* **1982**, *101*, 209–219.
12. Dubreuil, D.; Cleophax, J.; de Almeida, M. V.; Verre-Sebrié, C.; Liaigre, J.; Vass, G.; Gero, S. D. *Tetrahedron* **1997**, *53*, 16747–16766.
13. Salamci, E.; Secen, H.; Sütbeyaz, Y.; Balci, M. *J. Org. Chem.* **1997**, *62*, 2453–2457.
14. (a) Maezaki, N.; Nagahashi, N.; Yoshigami, R.; Iwata, C.; Tanaka, T. *Tetrahedron Lett.* **1999**, *40*, 3781–3784; (b) Angelaud, R.; Landais, Y. *J. Org. Chem.* **1996**, *61*, 5202–5203.