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Total Synthesis of Quercitols: (+)-*allo*-, (–)-*proto*-, (+)-*talo*-, (–)-*gala*-, (+)-*gala*-, *neo*-, and (–)-*epi*-Quercitol

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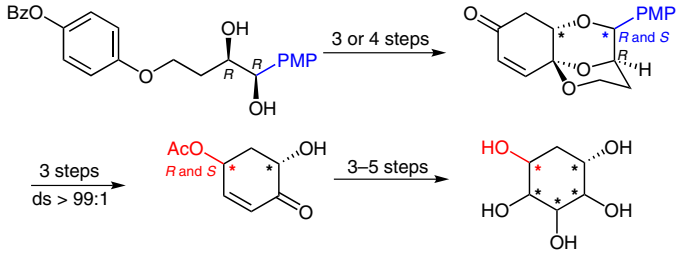

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Abstract The cyclohexenenones *exo*- and *endo*-**2** were converted into the cyclohexenyl acetates *exo*- and *endo*-**3** and *exo*- and *endo*-**5** with a diastereoselectivity of >99:1 (2 steps). Ether cleavage with DDQ in CH_2Cl_2/H_2O (20:1) and in situ ketal hydrolysis afforded the cyclohexenones **6** and **7** in up to 83% and 87% yield, respectively. Compound **6** was converted into (+)-*allo*- and (–)-*proto*-quercitol with a diastereoselectivity of 100:0 (4 steps). Moreover, **6** was carried on to (–)-*talo*-quercitol whereas **7** furnished the four remaining title quercitols (3–5 steps) including both enantiomers of *gala*-quercitol.

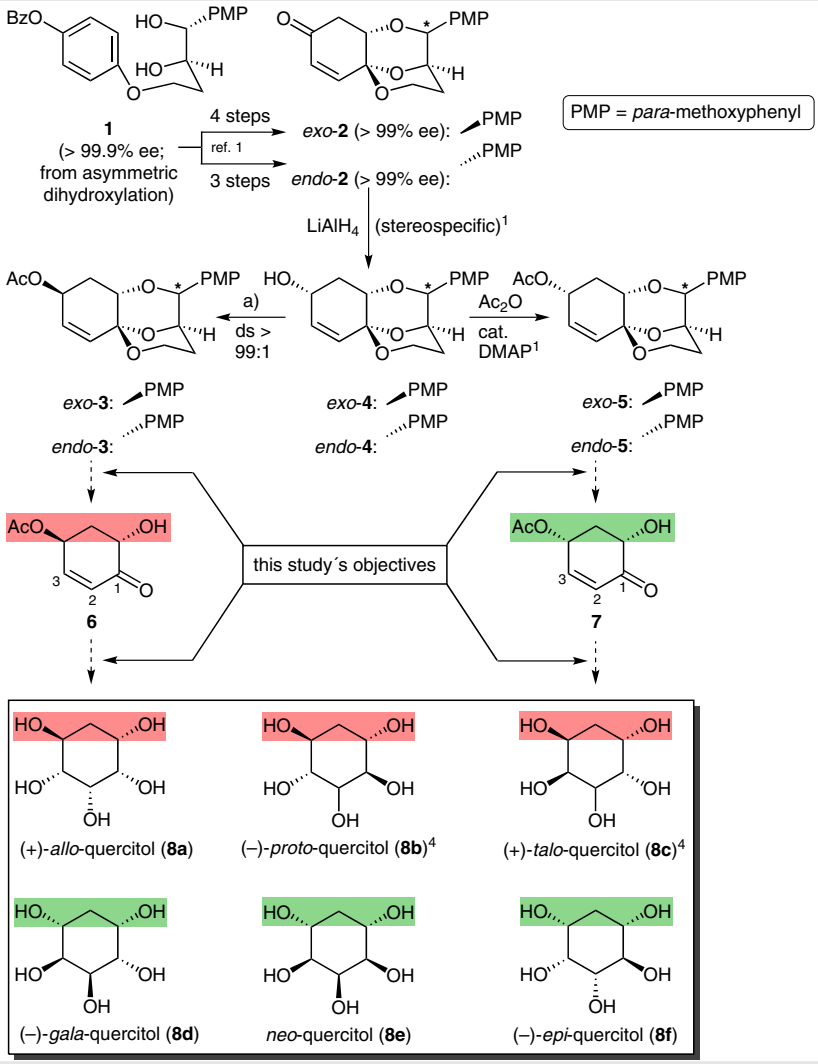
Key words cyclohexenones, diastereoselectivity, ether cleavage, α-hydroxy ketone, oxidation, reduction

Recently, we described six- and five-step syntheses, respectively, of the enantiomerically pure cyclohexenones *exo*-**2** and *endo*-**2** (Scheme 1).[1] Starting from hydroquinone monobenzoate and *trans*-4-(4-methoxyphenyl)but-3-en-1-ol, we prepared the enantiopure key intermediate diol **1** by a Mitsunobu etherification and an asymmetric Sharpless dihydroxylation. Elaborating the diol **1** into the cyclohexenones **2** entailed an oxidative cyclization with $PhI(O_2CCF_3)_2$ and an intramolecular *oxa*-Michael addition.

Upon treatment with $LiAlH_4$ the cyclohexenones *exo*- and *endo*-**2** afforded the cyclohexenols *exo*- and *endo*-**4** with perfect stereocontrol (Scheme 1).[1] The scaffolds, of which these substructures make part, allowed to dihydroxylate their C=C bonds and reduce their C=O bonds stereoselectively. This provided tricyclic cyclohexanetriol triacetates[1] **41** (for their formulas, see Scheme 8, footnote 14). They looked like precursors of cyclohexitols (= polyhydroxycyclohexanes and -hexenes) in general and of quercitols (= pentahydroxycyclohexanes) more specifically.[2]

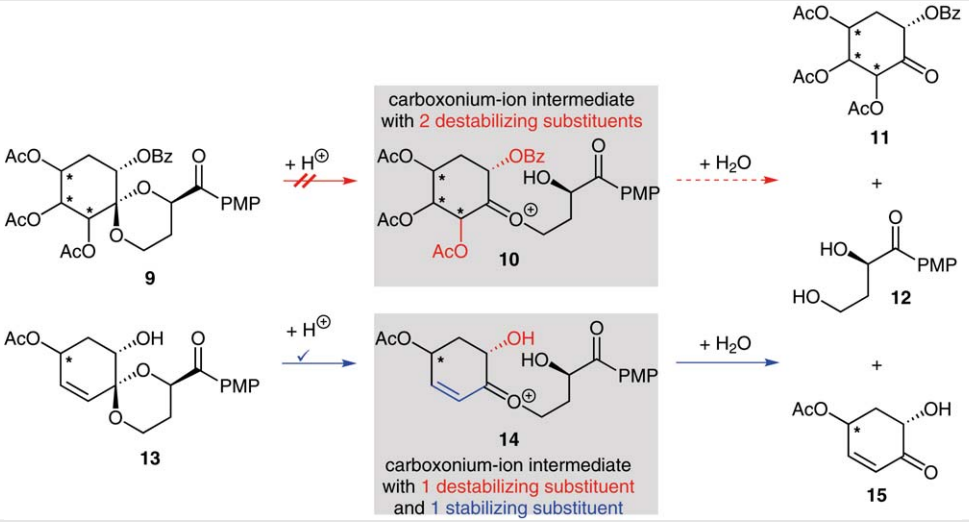
However, proceeding from **2**-based tricycles to quercitols required avoiding the tricyclic cyclohexanetriol triacetates mentioned above. Therefore, we reversed the originally anticipated order of C=C bond functionalization and protecting-group removal.[1] Accordingly, we began by transforming the cyclohexenols *exo*- and *endo*-**4** into the acetates *exo*- and *endo*-**3** under Mitsunobu conditions (inversion of configuration; this work, Scheme 1) and into the diastereomeric acetates *exo*- and *endo*-**5** by standard esterification (retention of configuration,[1] Scheme 1). We then cleaved their PMB ethers explicitly and the remaining ketal moieties *en passant* (see details below). This delivered the stereopure cyclohexenonediol monoacetates **6** and **7**. We created a glycol moiety from their C^2=C^3 bond and a hydroxy group from their C^1=O bond. The result was that the sp^2 centers of monoacetates **6** and **7** had given way to 1,2,3-triol motifs. Ammonolyses in methanol liberated (+)-*allo*-quercitol (**8a**),[3] (–)-*proto*-quercitol (**8b**[4]),[5] and (+)-*talo*-quercitol (**8c**[4])[6] from follow-up products of the cyclohexenonediol monoacetate **6**. Analogous ammonolyses released (–)-*gala*-quercitol (**8d**),[7] (+)-*gala*-quercitol (depicted in Scheme 6),[8] *neo*-quercitol (**8e**),[9] and (–)-*epi*-quercitol (**8f**)[10] from follow-up products of the diastereomeric cyclohexenonediol monoacetate **7**.

In our route to quercitols **8** we abolished the tricyclic cyclohexanetriol triacetates of our previous communication.[1] Instead, we took to the cyclohexenonediol monoacetates **6** and **7** as precursors. This change was caused by the following observations: Cleaving the benzylic C–O bond in the 1,4-dioxane moiety of several of the mentioned tricyclic cyclohexanetriol triacetates **41** with DDQ,[11–13] and benzoylation rendered ketone-substituted spiroketals **9** alright (Scheme 2; for details, see footnote 14). However, they marked dead-ends for our endeavor. This is because they could not be hydrolyzed to the underlying cyclohexanones **11**.[15] Their resilience is plausibly due to the destabilization of the carboxonium ion intermediate **10** – via which the hydrolysis of ketal **9** should proceed – by the acyloxy substituents highlighted in Scheme 2. Replacing one of them by an OH group and the other by a C=C bond the structure of carboxonium ion **14** is derived. Since an OH group is less electron withdrawing than an acyloxy substituent and a C=C bond other than an acyloxy substituent donates electron density, the carboxonium ion **14** should be more stable than **10**. From this consideration we inferred that type-**13** spiroketals might be amenable to hydrolyses.

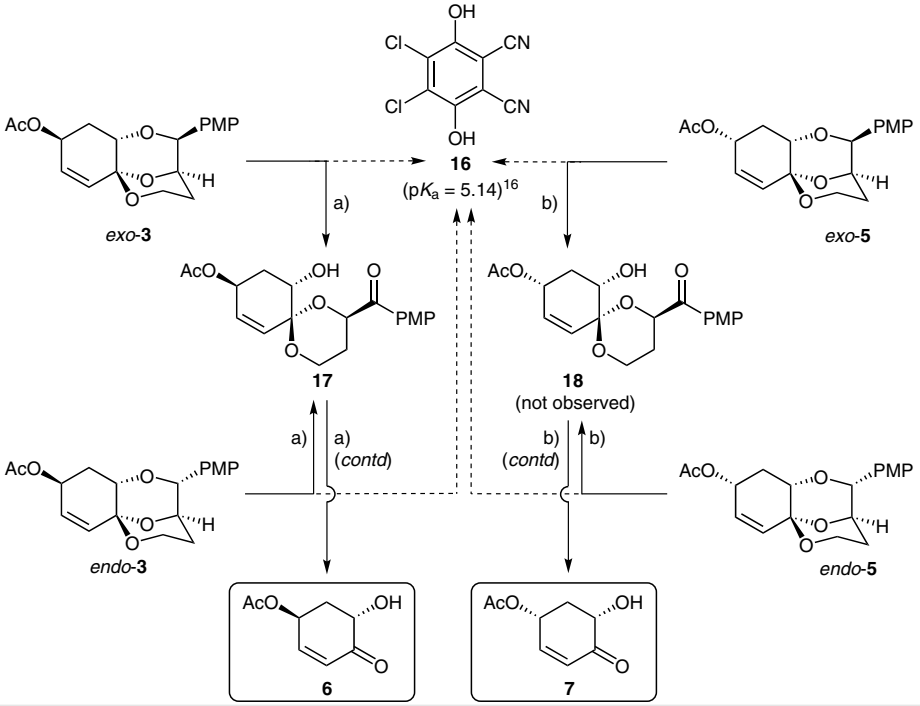


Scheme 1 Targeting quercitols **8** from the cyclohexenones *exo*- and *endo*-**2**[1] via the cyclohexenyl acetates *exo*- and *endo*-**3** (new; → **8a**–**c**) or *exo*- and *endo*-**5** (known;[1] → **8d**–**f**). *Reagents and conditions*: (a) For *exo*-**3**: AcOH (1.5 equiv), DIAD (1.3 equiv), Ph_3P (1.3 equiv), THF, r.t., 30 min; 91%. For *endo*-**3**: AcOH (1.5 equiv), DIAD (1.3 equiv), Ph_3P (1.3 equiv), THF, 0 °C, 15 min; 93%. DIAD = diisopropyl azodicarboxylate.

DDQ[11–13] in CH_2Cl_2/H_2O (20:1) cleaved the benzylic C–O bond in the respective 1,4-dioxane moiety of the tricyclic cyclohexenyl acetates *exo*-**3**/*endo*-**3** and *exo*-**5**/*endo*-**5** (Scheme 3). To our surprise as much as delight these substrates reacted beyond the type-**13** spiroketal stage. The only substrate, which rendered a spiroketal – besides nearly 70% overreaction – was *exo*-**3**; it gave 22% **17** after three days. The major product or exclusive products were the cyclohexenonediol monoacetates **6** (starting from **3**) and **7** (starting from **5**). This implies that the spiroketals **17** and **18**, which resulted along with one equivalent of the acidic[16] hydroquinone **16** from the oxidation step, hydrolyzed in situ in the water-containing reaction mixtures. Complete hydrolyses took six days starting from *exo*-**3** or *endo*-**3** (→ **6**) and three days starting from *exo*-**5** or *endo*-**5** (→ 7). The final products **6** and **7** were best obtained from *endo*-**3** (83% yield) and from *exo*-**5** (87% yield), respectively. They served as precursors of all quercitols obtained in the sequel. These were, from **6**: (+)-*allo*-quercitol (**8a**), (–)-*proto*-quercitol (**8b**, both Scheme 4), and (+)-*talo*-quercitol (**8c**, Scheme 5); from **7**: (–)-*gala*-quercitol (**8d**) plus (+)-*gala*-quercitol (*ent*-**8d**, both Scheme 6), *neo*-quercitol (**8e**), and (–)-*epi*-quercitol (**8f**, both Scheme 7).

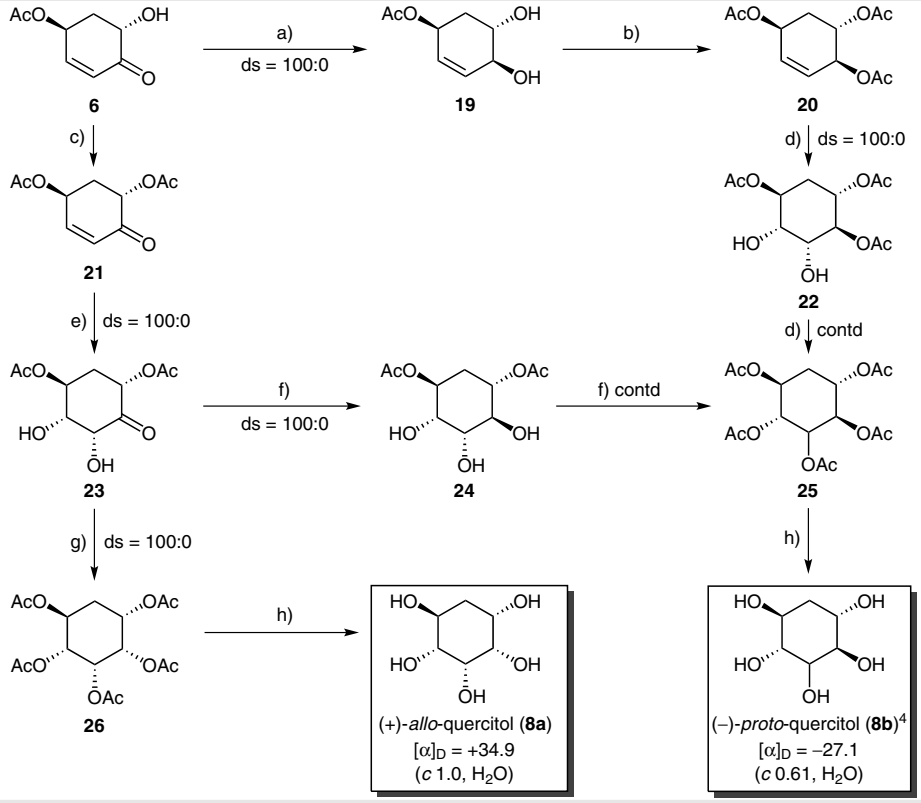


Scheme 2 Hydrolysis suppression vs. hydrolysis support by substituents with a –I vs. +M effect in the carboxonium ions **10** and **14**, respectively. Carboxonium ions **10** and **14** are expected to form in the rate-determining step of the elusive hydrolyses of type-**9** ketals (the preparation of which is described in footnote 14) vs. the ready hydrolyses of type-**13** ketals (the preparation of which became part of the present study).



Scheme 3 Deprotection of cyclohexenyl acetates **3** and **5** through DDQ-induced tandem oxidations (→ spiroketals **17** and **18**)/in situ hydrolyses (→ cyclohexenones **6** and **7**). *Reagents and conditions*: (a) DDQ (1.2 equiv), CH_2Cl_2/H_2O (20:1), r.t.; 27% **17**, <70% **6** (impure) from *exo*-**3** after 3 d; or no **17** and 81% **6** from *exo*-**3** after 6 d, respectively; 83% **6** from *endo*-**3** after 6 d. (b) DDQ (1.2 equiv), CH_2Cl_2/H_2O (20:1), r.t., 3 d; 87% **7** (from *exo*-**5**); 82% **7** (from *endo*-**5**). DDQ = dichlorodicyanobenzoquinone.

Scheme 4 shows how we converted the cyclohexenonediol monoacetate **6** with perfect stereoselectivity into (–)-*proto*-quercitol (**8b**) using either of two different pathways. They converged after three steps at (–)-*proto*-quercitol pentaacetate (**25**), and the latter furnished (–)-*proto*-quercitol (**8b**)[5] quantitatively by ammonolysis in methanol.[17–19] The pentaacetate **25** was reached from **6** either in 87% overall yield by the step order reduction (→ **19**), acetylation (→ **20**[20–22]), and dihydroxylation–acetylation, or in 39% overall yield by the step order acetylation (→ **21**), dihydroxylation (→ **23**), and reduction–acetylation. The dihydroxylations both of cyclohexene **20** and of cyclohexenone **21** were per-

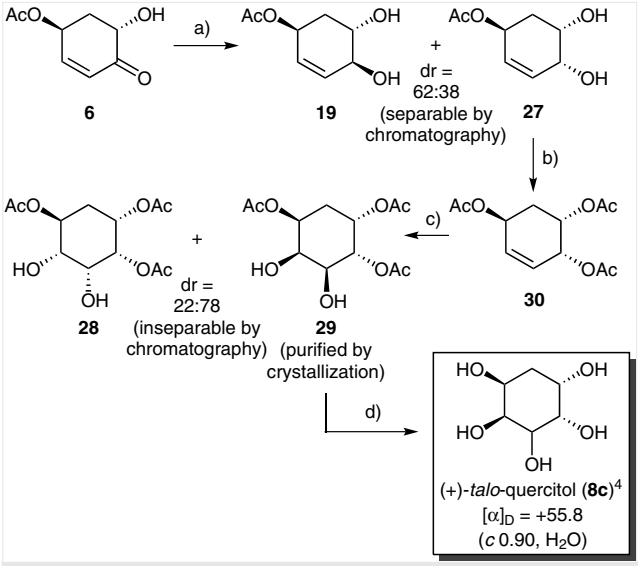


Scheme 4 Preparation of (+)-*allo*-quercitol (**8a**) and (–)-*proto*-quercitol (**8b**). *Reagents and conditions*: (a) $Me_4N^+{}^-BH(OAc)_3$ (2.0 equiv), AcOH (2.0 equiv), MeCN, 0 °C to r.t., 15 h; 91%. (b) Ac_2O (4.0 equiv), DMAP (20 mol%), pyridine (5.0 equiv), CH_2Cl_2, r.t., 20 h; 96%. (c) AcCl (1.5 equiv), DMAP (15 mol%), pyridine (2.0 equiv), CH_2Cl_2, r.t., 2 h; 87%. (d) $K_2OsO_2(OH)_4$ (5 mol%), citric acid (2.0 equiv), NMO (1.5 equiv), *t*-BuOH/H_2O (1:1), r.t., 1 h; Ac_2O (4.0 equiv), DMAP (20 mol-%), pyridine (5.0 equiv.), CH_2Cl_2, r.t., 15 h; 99%. (e) $K_2OsO_2(OH)_4$ (5 mol%), citric acid (2.0 equiv), NMO (1.5 equiv.), *t*-BuOH/H_2O (1:1), r.t., 2 h; 77%. (f) $Me_4N^+{}^-BH(OAc)_3$ (2.0 equiv), AcOH (4.0 equiv), MeCN, 0 °C to r.t., 5 h; aqueous workup; Ac_2O (28 equiv), DMAP (0.5 equiv), pyridine (34 equiv), THF, reflux, 15 h; 58%. (g) LiBH(*s*-Bu)$_3$ (4.0 equiv), THF, –78 °C to –10 °C, 5 h; Ac_2O (27 equiv), DMAP (0.5 equiv), r.t., 15 h; 71%. (h) NH_3 (gas), MeOH, r.t., 3 h; 100% (for **8a** and **8b**, respectively). DMAP = 4-(dimethylamino)pyridine; NMO = *N*-methylmorpholine-*N*-oxide.

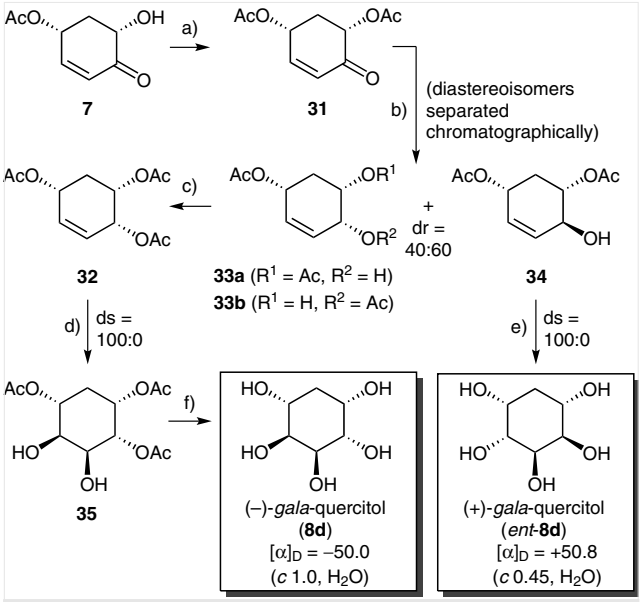
formed with Sharpless' OsO_4/NMO/citric acid protocol,[23] even if **20** would have subsided also to other oxidants.[24,25] Carbonyl reduction in either pathway to (–)-*proto*-quercitol pentaacetate (**25**) was effected using $Me_4N^+{}^-BH(OAc)_3$[26] as an 'OH-directable' reductant. The respective substrates, namely the cyclohexenone **6** and the cyclohexanone **23**, rendered exclusively the desired *trans*-1,2-diol units in the resulting cyclohexene **19** and cyclohexane **24**. This could be expected on grounds of literature precedence.[26]

The cyclohexanone **23** was a precursor not only of synthetic (–)-*proto*-quercitol (**8b**) but of synthetic (+)-*allo*-quercitol (**8a**),[3] too (Scheme 4). This is because LiBH(*s*-Bu)$_3$[27] reduced the cyclohexanone **23** with perfect stereocomplementarity relative to $Me_4N^+{}^-BH(OAc)_3$.[26] This reduction and an ensuing acetylation afforded 71% of the (+)-*allo*-quercitol pentaacetate **26**.[3] Ammonolysis[28] led to (+)-*allo*-quercitol (**8a**)[3] in 100% yield.[29]

Scheme 5 starts with the closest we came to a stereocomplementary reduction of the cyclohexenonediol monoacetate **6**. With $Me_4N^+{}^-BH(OAc)_3$,[26] **6** had given the *cis*-1,2-diol **19** selectively (Scheme 4). Indeed, whatever the reductant was, **19** formed preferentially. At best $NaBH_4/CaCl_2$[30] delivered a 62:38 mixture of the unavoidable *cis*-1,2-diol **19** and the desired *trans*-1,2-diol **27**. Separation by flash chromatography on silica gel[31] furnished 30% of the latter. After acetylation to the cyclohexene triacetate **30**,[32] dihydroxylation with OsO_4/NMO/citric acid[23] exhibited little stereocontrol. This was plausible since the allylic acetoxy groups flank the C=C bond of substrate **30** from opposite sides.[33] A 78:22 mixture of diastereomeric diols **29** and **28** resulted in 91% yield. Inseparable by flash chromatography,[31] the major diol **29** was obtained diastereomerically pure by crystallization from Et_2O in 67% yield. Its ammonolysis delivered (+)-*talo*-quercitol (**8c**)[6] in 98% yield.[18,34]



Scheme 5 Preparation of (+)-*talo*-quercitol (**8c**). *Reagents and conditions*: (a) $NaBH_4$ (0.5-fold molar amount), $CaCl_2$ (1.0 equiv), MeOH, –20 °C, 30 min; 50% **19** and 30% **27** after separation by flash chromatography. (b) Ac_2O (4 equiv), DMAP (15 mol%), pyridine (6 equiv), CH_2Cl_2, r.t., 3 h; 94%. (c) $K_2OsO_2(OH)_4$ (5 mol%), citric acid (2.0 equiv), NMO (1.5 equiv), *t*-BuOH/H_2O (1:1), r.t., 2 h; 91% of a 22:78 mixture of **28** and **29**; the latter (67% yield) was obtained diastereomerically pure by crystallization from Et_2O, whereas **28** (86:14 dr, 23% yield) was isolated from the mother liquors. (d) NH_3 (gas), MeOH, r.t., 1 h; 98%.

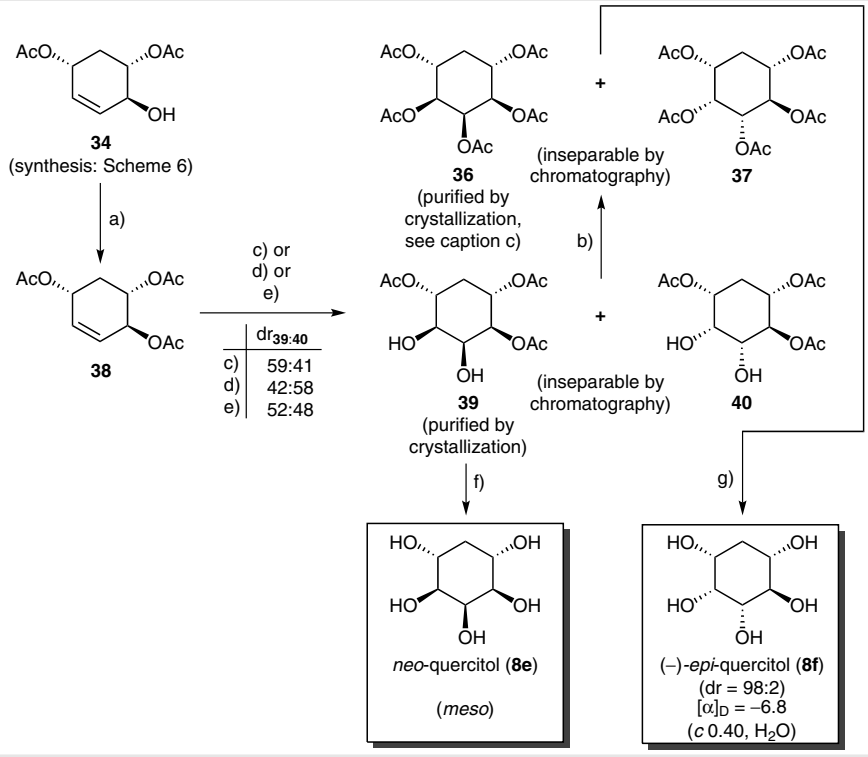


Scheme 6 Preparation of both enantiomers of *gala*-quercitol (**8d**). *Reagents and conditions*: (a) AcCl (1.5 equiv), DMAP (15 mol%), pyridine (2.0 equiv), CH_2Cl_2, r.t., 2 h; 82%. (b) $NaBH_4$ (0.4-fold molar amount), MeOH, –20 °C, 45 min; 38% of an inseparable 43:57 mixture of **33a** and **33b** chromatographically separated from 57% **34**. (c) Ac_2O (2.0 equiv), DMAP (15 mol%), pyridine (3.0 equiv), CH_2Cl_2, r.t., 6 h; 98%. (d) $K_2OsO_2(OH)_4$ (5 mol%), citric acid (2.0 equiv), NMO (1.5 equiv), *t*-BuOH/H_2O (1:1), r.t., 1 h; 99%. e) H_2O_2 (30% aqueous solution, 3.8 equiv), HCO_2H, r.t., 2 d; NH_3 (gas), MeOH, r.t., 3 h; 98%. (f) NH_3 (gas), MeOH, r.t., 2 h; 94%.

The cyclohexenonediol monoacetate **7** allowed us to embark on the pair of quercitol syntheses shown in Scheme 6. They provide, as one desires, either (–)-*gala*-quercitol (**8d**) or (+)-*gala*-quercitol (*ent*-**8d**) and are 'enantiodivergent' therefore. The diacetate **31**, prepared from monoacetate **7** in 82% yield, and $NaBH_4$ reacted to give a mixture of alcohols. It contained a major diastereomer **34**, a minor diastereomer **33a**, and its 'regioisomer' **33b**, which resulted from **33a** by an acyl shift. Flash chromatography on silica gel[31] rendered the diacetate **34** in 57% yield and a 43:57 mixture of the 'regioisomeric' diacetates **33a** and **33b** in 38% yield; acetylation allowed this mixture to converge as triacetate **32**[35–37] (98% yield).

Finishing our synthetic quercitols **8d** and *ent*-**8d** required dihydroxylating the C=C bond of triacetate **32** *cis*-selectively and the C=C bond of diacetate **34** *trans*-selectively (Scheme 6). The *cis*-dihydroxylation of triacetate **32** was accomplished by the OsO_4/NMO/citric acid procedure of Sharpless et al.[23]. As a single product we obtained glycol **35**[38,39] (99% yield). Its ammonolysis furnished (–)-*gala*-quercitol (**8d**[6a–c,7]) in 94% yield.[40] The *trans*-dihydroxylation of diacetate **34** was realized with H_2O_2 (30%) in formic acid.[41] This mixture reacts by peracid formation, epoxidation, S_N2 ring opening by HCO_2H, and subsequent (partial) formylation of OH groups.[42] The resulting mixture was ammonolyzed to isolate (+)-*gala*-quercitol (*ent*-**8d**)[8] as a single diastereoisomer in 98% yield.[43]

The cyclohexenetriol diacetate **34** (preparation: Scheme 6) was coerced into giving two further quercitols. As detailed in Scheme 7, this started with forming the corresponding cyclohexenetriol triacetate **38**. If a diastereoselective *cis*-dihydroxylation of its C=C bond had been possible, we would have advanced readily to *neo*-quercitol (**8e**) or to (–)-*epi*-quercitol (**8f**). Such diastereoselectivities remained elusive, however. The present study rather underscores that *cis*-*vic*-dihydroxylations of cyclohexenes, which contain two allylic O–H or O–acyl substituents, are highly diastereoselective only if they are *cis* substituents, yet lack diastereocontrol otherwise. This is illustrated by the dihydroxylations of cyclohexenes **20** (Scheme 4) and **32** (Scheme 6) vs. **30** (Scheme 5) and **38** (Scheme 7): A dihydroxylation of the cyclohexene **38** by the OsO_4/NMO/citric acid protocol[23] provided a 59:41 mixture (98% of the diastereomeric diols **39** and **40**).[44] This ratio did not change substantially when the cyclohexene **38** was subjected to Sharpless' asymmetric dihydroxylation conditions:[45] In the presence of $(DHQ)_2PHAL$ (ingredient of AD-mix α[45a,b]) and $NaHCO_3$ a mixture of diols **39** and **40** resulted, which, after acetylation of the crude product, gave a 42:58 mixture[46]) of pentaacetates **36**[8b,9e] and **37**.[7f,47] Employing $(DHQD)_2PHAL$ (ingredient of AD-mix β[45a,b]), a 52:48 mixture of the pentaacetates **36** and **37** was obtained.[48]



Scheme 7 Preparation of *neo*-quercitol (**8e**) and (–)-*epi*-quercitol (**8f**). *Reagents and conditions*: (a) Ac_2O (2.0 equiv), DMAP (15 mol%), pyridine (3.0 equiv), CH_2Cl_2, r.t., 6 h; 98%. (b) For a 59:41 mixture of **39** and **40**: Ac_2O (8 equiv), DMAP (15 mol%), pyridine (12 equiv), CH_2Cl_2, r.t., 15 h; 98% of a 59:41 mixture of **36** and **37**, from which only **36** (54% yield) was obtained diastereomerically pure by crystallization from Et_2O–pentane (1:2), whereas **37** (93:7 dr, 44% yield) was isolated from the mother liquors. (c) $K_2OsO_2(OH)_4$ (5 mol%), citric acid (2.0 equiv), NMO (1.5 equiv), *t*-BuOH/H_2O (1:1), r.t., 1 h; 98% of a 59:41 mixture of **39** and **40**, from which **39** was obtained diastereomerically pure by crystallization from Et_2O. (d) $K_2OsO_2(OH)_4$ (2 mol%), $(DHQ)_2PHAL$ (4 mol%), $PhSO_2NH_2$ (1.0 equiv), $K_3Fe(CN)_6$ (3.0 equiv), K_2CO_3 (3.0 equiv), $NaHCO_3$ (3.0 equiv), *t*-BuOH/H_2O (1:1), 0 °C, 5 d; 16% of starting material recovered by chromatography; acetylation of crude product: Ac_2O, DMAP, pyridine, CH_2Cl_2, r.t., 15 h; 27% of a 42:58 mixture of **36** and **37**.[46] (e) Same as (d), but $(DHQD)_2PHAL$ (4 mol%) instead of $(DHQ)_2PHAL$; 28% of a 52:48 mixture of **36** and **37**, 10% of starting material recovered by chromatography. (f) NH_3 (gas), MeOH, r.t., 1 h; 100%. (g) Starting from a 93:7 mixture of **37** and **36**: NH_3 (gas), MeOH, r.t., 1 h; crude product: 97% of a 93:7 mixture of **8f** and **8e**; after crystallization from MeOH: 73% of a 98:2 mixture of **8f** and **8e**.

The diols **39** and **40** were inseparable by flash chromatography on silica gel;[31] gratifyingly, the major diol **39** crystallized from Et_2O diastereomerically pure (Scheme 7). Its ammonolysis provided *neo*-quercitol (**8e**)[9] diastereomerically pure in quantitative yield.[49,50] Acetylation of the 59:41 mixture of the diastereomeric diols **39** and **40** (obtained by the OsO_4/NMO/citric acid protocol) gave a 59:41 mixture of the corresponding pentaacetates **36** and **37**.[47] Crystallization from Et_2O gave the pure major pentaacetate **36** in 54% yield; the mother liquors rendered the minor pentaacetate **37** with 93:7 diasteromeric ratio in 44% yield. Ammonolysis of this compound followed by crystallization from methanol gave (–)-*epi*-quercitol (**8f**)[10] with 98:2 diasteromeric ratio in 73% yield.[49,51]

We demonstrated that the tricyclic cyclohexenones *exo*-**2** and *endo*-**2** are progenitors of the cyclohexenonediol monoacetates **6** and **7**. These, compounds in turn, served as progenitors of three dextrorotatory quercitols (**8a**, **8c**, *ent*-**8d**), three levorotatory quercitols (**8b**, **8d**, **8f**), and one *meso*-configured quercitol (**8e**).[52] The underlying transformations were often, but not always, highly stereoselective. Stereocontrol might improve if the C=C bond functionalizations could be performed prior to cleaving the tricyclic scaffold. With that goal in mind it might be worthwhile to investigate the reductive cleavage of the C–O bond of all tricyclic PMB ethers, at which we had not looked previously.[1,15]

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379603.

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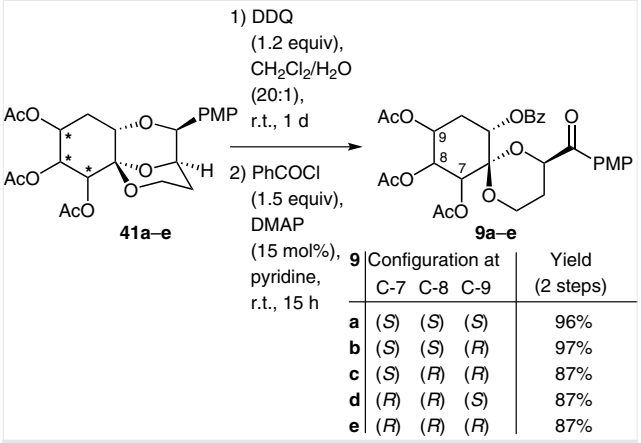
(4) C-3 of this compound represents a chirotopic nonstereogenic center. Because of the latter attribute it suffices to connect C-3 and 3-OH by an 'ordinary bond' rather than by a wedge or by hatches.
(5) Syntheses of (–)-*proto*-quercitol (**8b**): (a) McCasland, G. E.; Naumann, M. O.; Durham, L. J. *J. Org. Chem.* **1968**, *33*, 4220. (b) Angyal, S. J.; Odier, L. *Carbohydr. Res.* **1982**, *101*, 209. (c) Gültekin, M. S.; Çelik, M.; Turkut, E.; Tanyeli, C.; Balci, M. *Tetrahedron: Asymmetry* **2004**, *15*, 453; corrigendum: *Tetrahedron: Asymmetry* **2004**, *15*, 1959.
(6) Syntheses of (+)-*talo*-quercitol (**8c**): (a) McCasland, G. E.; Furuta, S.; Johnson, L. F.; Shoolery, J. N. *J. Am. Chem. Soc.* **1961**, *83*, 2335. (b) Angelaud, R.; Babot, O.; Charvat, T.; Landais, Y. *J. Org. Chem.* **1999**, *64*, 9613. (c) Hydloft, L.; Madsen, R. *J. Am. Chem. Soc.* **2000**, *122*, 8444. (d) Ref. 3.
(7) Syntheses of (–)-*gala*-quercitol (**8d**): (a) Ref. 6a. (b) Dubreuil, D.; Cleophax, J.; Vieira de Almeida, M.; Verre-Sebrié, C.; Liaigre, J.; Vass, G.; Gero, S. D. *Tetrahedron* **1997**, *53*, 16747. (c) Ref. 6b. (d) Maezaki, N.; Nagahashi, N.; Yoshigami, R.; Iwata, C.; Tanaka, T. *Tetrahedron Lett.* **1999**, *40*, 3781. (e) Ref. 6c. (f) Shih, T.-L.; Lin, Y.-L. *Synth. Commun.* **2005**, *35*, 1809. (g) Murugan, A.; Yadav, A. K.; Gurjar, M. K. *Tetrahedron Lett.* **2005**, *46*, 6235.
(8) Syntheses of (+)-*gala*-quercitol (*ent*-**8d**): (a) Ref. 5b. (b) Shih, T.-L.; Lin, Y.-L.; Kuo, W.-S. *Tetrahedron* **2005**, *61*, 1919.
(9) Syntheses of *neo*-quercitol (**8e**): (a) Ref. 5b. (b) Kühlmeyer, R.; Keller, R.; Schwesinger, R.; Netscher, T.; Fritz, H.; Prinzbach, H. *Chem. Ber.* **1984**, *117*, 1765. (c) Ref. 8b. (d) Murali, C.; Gurale, B. P.; Shashindhar, M. S. *Eur. J. Org. Chem.* **2010**, 755. (e) Aydin, G.; Savran, T.; Aktaş, F.; Baran, A.; Balci, M. *Org. Biomol. Chem.* **2013**, *11*, 1511.
(10) Syntheses of (–)-*epi*-quercitol (**8f**): (a) Ref. 7b. (b) Biamonte, M. A.; Vasella, A. *Helv. Chim. Acta* **1998**, *81*, 688. (c) Horne, G.; Potter, B. V. L. *Chem. Eur. J.* **2001**, *7*, 80. (d) Ref. 7f; therein **8f** was referred to as dextrorotatory. In accordance therewith, synthetic *ent*-**8f** was referred to as levorotatory in ref. 8b. The two findings disagree with our synthetic **8f** being levorotatory (Scheme 7).
(11) DDQ oxidations of *primary* PMB ethers of primary or secondary alcohols giving *p*-methoxybenzaldehyde plus these alcohols: Oikawa, Y.; Yoshioka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1982**, *23*, 885.
(12) DDQ oxidations of secondary PMB ethers (specifically: *p*-methoxybenzhydryl ethers) of primary alcohols giving *p*-methoxybenzophenone plus these alcohols: Sharma, G. V. M.; Prasad, T. R.; Rakesh, S. B. *Synth. Commun.* **2004**, *34*, 941.
(13) DDQ oxidations of *secondary* PMB esters of carboxylic acids giving *p*-methoxyacetophenone plus these carboxylic acids: Yoo, S.-E.; Kim, H. R.; Yi, K. Y. *Tetrahedron Lett.* **1990**, *31*, 5913.
(14) The benzylic C–O bond in the 1,4-dioxane moieties of the tricyclic cyclohexanetriol triacetates[1] **41** was cleaved with DDQ in CH_2Cl_2/H_2O (20:1), and the resulting alcohols were benzoylated. This provided the nonhydrolyzable spiroketals **9a**–**e** in overall yields around 90% (Scheme 8).



9	Configuration at C-7	C-8	C-9	Yield (2 steps)
a	(*S*)	(*S*)	(*S*)	96%
b	(*S*)	(*S*)	(*R*)	97%
c	(*S*)	(*R*)	(*R*)	87%
d	(*R*)	(*R*)	(*S*)	87%
e	(*R*)	(*R*)	(*R*)	87%

Scheme 8

(15) (a) In the tricyclic cyclohexanetriol triacetate **41b** (which now rendered the spiroketal **9b** by oxidative cleavage as depicted in Scheme 8) we had been able to cleave[1] the benzylic C–O bond by an ionic hydrogenolysis with Et_3SiH/F_3CCO_2H.[15b] We then effected a benzylic bromination, whereupon treatment with Zn induced a reductive elimination; it ring-opened the spiroketal moiety.[1] The scope and limitations of *that* approach have not yet been investigated. (b) Ma, Z.; Hu, H.; Xiong, W.; Zhai, H. *Tetrahedron* **2007**, *63*, 7523.
(16) pK_{a1} of DDQ-H_2 (**16**): Akutagawa, T.; Saito, G. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1753.
(17) Ammonolysis of pentaacetate *rac*-**25**: see ref. 22c.
(18) In the present work we terminated the synthesis of each quercitol by an ammonolysis, the substrate of which was a pentaacetate (Scheme 4: **25** → **8g**, **26** → **8a**; Scheme 7: **37** → **8f**), a triacetate (Scheme 5: **29** → **8c**; Scheme 6: **35** → **8d**; Scheme 7: **39** → **8e**) or a mixed oligocarboxylate (Scheme 6; post-**34** → *ent*-**8d**). Each ammonolysis was executed under conditions described by Balci et al.[22c] for two analogous ammonolyses.
(19) **NMR Data of (–)-*proto*-Quercitol (8b, Figure 1)**
^{1}H NMR (500 MHz, D_2O): δ = 1.80 (ddd, J_{gem} = 14.0 Hz, $J_{6\text{-Hax},1}$ = 11.7 Hz, $J_{6\text{-Hax},5}$ = 3.1 Hz, 1 H, 6-H_{ax}), 1.98 (dddd, J_{gem} = 14.0 Hz, $J_{6\text{-Heq},1}$ = 4.8 Hz, $J_{6\text{-Heq},5}$ = 3.3 Hz, $^4J_{6\text{-Heq},4}$ = 1.2 Hz, 1 H, 6-H_{eq}), 3.55 (dd, $J_{2,3}$ = 9.7 Hz, $J_{2,1}$ = 9.1 Hz, 1 H, 2-H), 3.70 (dd, $J_{3,2}$ = 9.7 Hz, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 3.74 (ddd, $J_{1,6\text{-Hax}}$ = 11.7 Hz, $J_{1,2}$ = 9.1 Hz, $J_{1,6\text{-Heq}}$ = 4.8 Hz, 1 H, 1-H), 3.92 (ddd, $J_{4,5}$ = 3.6 Hz, $J_{4,3}$ = 3.3 Hz, $^4J_{4,6\text{-Heq}}$ = 1.2 Hz, 1 H, 4-H), 4.01 (ddd, $J_{5,4}$ = 3.6 Hz, $J_{5,6\text{-Heq}}$ = 3.3 Hz, $J_{5,6\text{-Hax}}$ = 3.1 Hz, 1 H, 5-H) ppm.

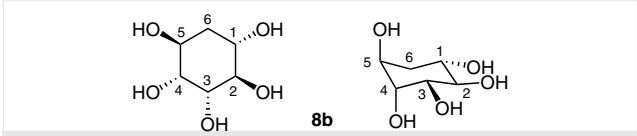


Figure 1

(20) Preparation of cyclohexenetriol triacetate **20** from cyclohexa-1,4-diene by an oxidation to *endo*-peroxide/hydroperoxide and an enzymatic kinetic resolution: see ref. 5c.
(21) Preparation of cyclohexenetriol triacetate *ent*-**20** from D-(–)-quinic acid: Shih, T.-L.; Kuo, W.-S.; Lin, Y.-L. *Tetrahedron Lett.* **2004**, *45*, 5751.
(22) Syntheses of cyclohexenetriol triacetate *rac*-**20** from cyclohexa-1,4-diene: (a) Seçen, H.; Salamci, E.; Sütbeyaz, Y.; Balci, M. *Synlett* **1993**, 609. (b) Gültekin, M. S.; Salamci, E.; Balci, M. *Car-*

bohydr. Res. **2003**, *338*, 1615. (c) Salamci, E.; Seçen, H.; Sütbeyaz, Y.; Balci, M. *J. Org. Chem.* **1997**, *62*, 2453. (d) Salamci, E.; Seçen, H.; Sütbeyaz, Y.; Balci, M. *Synth. Commun.* **1997**, *27*, 2223.

(23) Method: Dupau, P.; Epple, R.; Thomas, A. A.; Fokin, V. V.; Sharpless, K. B. *Adv. Synth. Catal.* **2002**, *344*, 421.

(24) Dihydroxylation of cyclohexenetriol triacetate **20** with OsO_4/*N*-methylmorpholine-*N*-oxide: see ref. 5c.

(25) Dihydroxylations of cyclohexenetriol triacetates *ent*-**20** and *rac*-**20** with $KMnO_4$: see ref. 21, 22a,c.

(26) OH-Directed triacetoxyborohydride reductions of β-hydroxyketones were studied in depth by (a) Evans, D. A.; Chapman, K. T. *Tetrahedron Lett.* **1986**, *27*, 5939. (b) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560. OH-Directed diastereoselective triacetoxyborohydride reduction of an α-hydroxycyclohexenone: (c) Bao, X.; Cao, Y.-X.; Chu, W.-D.; Qu, H.; Du, J.-Y.; Zhao, X.-H.; Ma, X.-Y.; Wang, C.-T.; Fan, C.-A. *Angew. Chem. Int. Ed.* **2013**, *52*, 14167. OH-Directed diastereoselective triacetoxyborohydride reduction of an α-hydroxybicyclo[2.2.2]octanone: (d) Griffith, D. R.; Botta, L.; St Denis, T. G.; Snyder, S. A. *J. Org. Chem.* **2014**, *79*, 88. OH-Directed diastereoselective triacetoxyborohydride reduction of a 4-hydroxydihydro-2*H*-pyran-3(4*H*)-one: (e) Shangguan, N.; Kiren, S.; Williams, L. J. *Org. Lett.* **2007**, *9*, 1093.

(27) Example for stereocomplementary diastereoselective α-hydroxycyclohexanone reductions with LiBH(*s*-Bu)$_3$ vs. triacyloxyborohydride: Breit, B.; Bigot, A. *Chem. Commun.* **2008**, 6498.

(28) The ammonolysis of the pentaacetate *ent*-**26** was described in ref. 8b.

(29) **NMR Data of (+)-*allo*-Quercitol (8a, Figure 2)**
^{1}H NMR (500 MHz, D_2O; 323 K): δ = 1.59 (ddd, J_{gem} = 14.1 Hz, $J_{6\text{-Hax},5}$ = 9.4 Hz, $J_{6\text{-Hax},1}$ = 3.3 Hz, 1 H, 6-H$_{ax}$), 2.12 (ddd, J_{gem} = 14.1 Hz, $J_{6\text{-Heq},1}$ = 6.1 Hz, $J_{6\text{-Heq},5}$ = 4.4 Hz, 1 H, 6-H$_{eq}$), 3.56 (dd, $J_{4,5}$ = 8.0 Hz, $J_{4,3}$ = 3.1 Hz, 1 H, 4-H), 3.79 (dd, $J_{2,3}$ = 3.1 Hz, $J_{2,1}$ = 3.1 Hz, 1 H, 2-H), 4.01 (ddd, $J_{3,2}$ = 3.1 Hz, $J_{3,4}$ = 3.1 Hz, $^4J_{3,1}$ = 1.3 Hz, 1 H, 3-H), 4.03 (ddd, $J_{5,6\text{-Hax}}$ = 9.4 Hz, $J_{5,4}$ = 8.0 Hz, $J_{5,6\text{-Heq}}$ = 4.4 Hz, 1 H, 5-H), 4.05 (dddd, $J_{1,6\text{-Heq}}$ = 6.1 Hz, $J_{1,6\text{-Hax}}$ = 3.3 Hz, $J_{1,2}$ = 3.1 Hz, $^4J_{1,3}$ = 1.3 Hz, 1 H, 1-H) ppm.

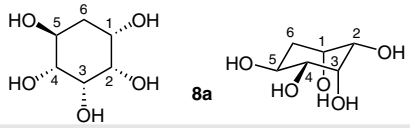


Figure 2

(30) Method: Fujii, H.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1991**, 1847.

(31) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(32) Synthesis of cyclohexenetriol triacetate **30** by an asymmetric eliminative epoxide opening: de Sousa, S. E.; O'Brien, P.; Pilgram, C. D. *Tetrahedron* **2002**, *58*, 4643.

(33) Dihydroxylations of cyclohexenetriol triacetate *ent*-**30** with $KMnO_4$ or RuO_4 gave an almost 1:1 ratio of the corresponding glycols *ent*-**28** and *ent*-**29**; after peracetylation, the combined overall yield was 74%, see ref. 8b.

(34) **NMR Data of (+)-*talo*-Quercitol (8c, Figure 3)**
^{1}H NMR (500 MHz, D_2O, 313 K): δ = 1.82–1.92 (m, 2 H, 6-H$_2$), 3.71 (dd, $J_{4,3}$ = 9.9 Hz, $J_{4,5}$ = 3.1 Hz, 1 H, 4-H), 3.75 (dd, $J_{3,4}$ = 9.9 Hz, $J_{3,2}$ = 2.7 Hz, 1 H, 3-H), 3.99 (ddd, $J_{1,6\text{-Hax}}$ = 10.6 Hz, $J_{1,6\text{-Heq}}$ = 5.9 Hz, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H), 4.03 (ddd, $J_{2,1}$ = 2.8 Hz, $J_{2,3}$ = 2.7 Hz, $^4J_{2,6\text{-Heq}}$ = 1.2 Hz, 1 H, 2-H), 4.07 (ddd, $J_{5,6\text{-Heq}}$ = 3.3 Hz, $J_{5,6\text{-Hax}}$ = 3.3 Hz, $J_{5,4}$ = 3.3 Hz, 1 H, 5-H) ppm.

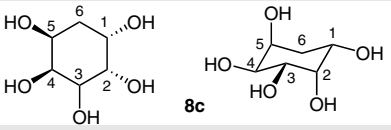


Figure 3

(35) For a different synthesis of cyclohexenetriol triacetate **32**: see ref. 32.

(36) Synthesis of cyclohexenetriol triacetate *ent*-**32** from D-(–)-quinic acid: see ref. 8b.

(37) Synthesis of cyclohexenetriol triacetate *rac*-**32** from cyclohexa-1,4-diene: see ref. 22c.

(38) Dihydroxylation of cyclohexenetriol triacetate *rac*-**32** with OsO_4/NMO: see ref. 22c.

(39) Dihydroxylations of cyclohexenetriol triacetate *ent*-**32** with $KMnO_4$ or RuO_4: see ref. 8b.

(40) **NMR Data of (–)-*gala*-Quercitol (8d, Figure 4)**
^{1}H NMR (500 MHz, D_2O): δ = 1.72 (ddd, J_{gem} = 12.3 Hz, $J_{6\text{-Hax},5}$ = 11.4 Hz, $J_{6\text{-Hax},1}$ = 10.6 Hz, 1 H, 6-H$_{ax}$), 2.00 (dddd, J_{gem} = 12.3 Hz, $J_{6\text{-Heq},1}$ = 4.6 Hz, $J_{6\text{-Heq},5}$ = 4.4 Hz, $^4J_{6\text{-Heq},4}$ = 1.3 Hz, 1 H, 6-H$_{eq}$), 3.67 (dd, $J_{2,1}$ = 9.1 Hz, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 3.79 (ddd, $J_{1,6\text{-Hax}}$ = 10.6 Hz, $J_{1,2}$ = 9.1 Hz, $J_{1,6\text{-Heq}}$ = 4.6 Hz, 1 H, 1-H), 3.92 (ddd, $J_{4,3}$ = 4.3 Hz, $J_{4,5}$ = 3.1 Hz, $^4J_{4,6\text{-Heq}}$ = 1.3 Hz, 1 H, 4-H), 4.00 (dd, $J_{3,4}$ = 4.3 Hz, $J_{3,2}$ = 3.2 Hz, 1 H, 3-H), 4.01 (ddd, $J_{5,6\text{-Hax}}$ = 11.4 Hz, $J_{5,6\text{-Heq}}$ = 4.4 Hz, $J_{5,4}$ = 3.1 Hz, 1 H, 5-H) ppm.

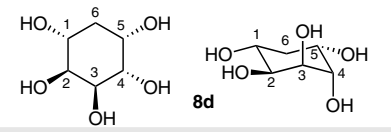
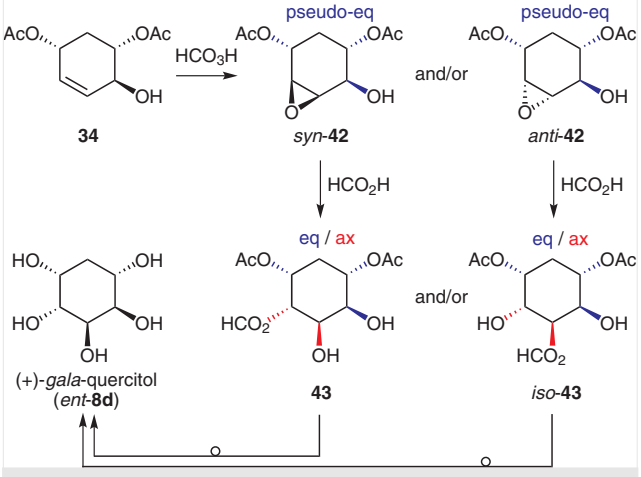


Figure 4

(41) Method: (a) Adkins, H.; Roebuck, A. K. *J. Am. Chem. Soc.* **1948**, *70*, 4041. (b) Ogawa, S.; Aoki, Y.; Takagaki, T. *Carbohydr. Res.* **1987**, *164*, 499. (c) Doddi, V. R.; Kumar, A.; Vankar, Y. D. *Tetrahedron* **2008**, *54*, 9117.

(42) In principle, the epoxidation of cyclohexenol **34** may lead to the *syn*- and/or the *anti*-epoxide (Scheme 9). If the Fürst–Plattner rule is respected, the ring opening of either epoxide should deliver the respective 'diaxially substituted dihydroxyformate' initially, that is, compounds **43** and *iso*-**43**, respectively. In the sequel, each of these dihydroxyformates would furnish (+)-*gala*-quercitol (*ent*-**8d**).



Scheme 9

(43) **NMR Data of (+)-*gala*-Quercitol (*ent*-8d, Figure 5)**

^{1}H NMR (500 MHz, CD_3OD): δ = 1.77 (ddd, J_{gem} = 12.3 Hz, $J_{6\text{-Hax},1}$ = 10.4 Hz, $J_{6\text{-Hax},5}$ = 10.4 Hz, 1 H, 6-H_{ax}), 1.90 (dddd, J_{gem} = 12.3 Hz, $J_{6\text{-Heq},1}$ = 4.4 Hz, $J_{6\text{-Heq},5}$ = 4.4 Hz, $^4J_{6\text{-Heq},2}$ = 1.2 Hz, 1 H, 6-H_{eq}), 3.64 (dd, $J_{4,5}$ = 8.5 Hz, $J_{4,3}$ = 3.2 Hz, 1 H, 4-H), 3.73 (ddd, $J_{5,6\text{-Hax}}$ = 10.0 Hz, $J_{5,4}$ = 8.6 Hz, $J_{5,6\text{-Heq}}$ = 4.4 Hz, 1 H, 5-H), 3.81 (dd, $J_{2,3}$ = 5.0 Hz, $J_{2,1}$ = 2.9 Hz, 1 H, 2-H), 3.91 (dd, $J_{3,2}$ = 5.0 Hz, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 3.95 (ddd, $J_{1,6\text{-Hax}}$ = 10.6 Hz, $J_{1,6\text{-Heq}}$ = 4.4 Hz, $J_{1,2}$ = 2.9 Hz, 1 H, 1-H) ppm.

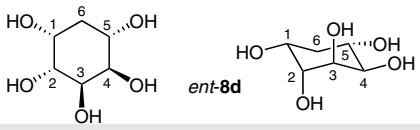


Figure 5

(44) Dihydroxylations of cyclohexenetriol triacetate *ent*-**38** with $KMnO_4$ or RuO_4 provided the glycols *ent*-**39** and *ent*-**40** with dr = 58:42 in 65% and 77% combined yield, respectively; see ref. 8b.

(45) First descriptions of the AD-mix protocols: (a) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768; (in the presence of $MeSO_2NH_2$). (b) See footnote 6 in: Jeong, K.-S.; Sjö, P.; Sharpless, K. B. *Tetrahedron Lett.* **1992**, *33*, 3833; (in the absence of $MeSO_2NH_2$). Recent reviews: (c) Zaitsev, A. B.; Adolfsson, H. *Synthesis* **2006**, 1725. (d) Noe, M. C.; Letavic, M. A.; Snow, S. L.; McCombie, S. *Org. React.* **2005**, *66*, 109. (e) Kolb, H. C.; Sharpless, K. B. In *Transition Metals for Organic Synthesis*; Vol. 2; Beller, M.; Bolm, C., Eds.; Wiley-VCH: Weinheim, **2004**, 275–298.

(46) The relative amounts of the quercitol pentaacetates **36** and **37** were determined from the integrals over non-overlapping ^{1}H NMR signals (400 MHz, $CDCl_3$) of this mixture. Their resonances are printed in boldface in the following enumerations:

NMR Data of Pentaacetate 36

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (dt, J_{gem} = 12.5 Hz, $J_{6\text{-Hax},1}$ = $J_{6\text{-Hax},5}$ = 11.7 Hz, 1 H, 6-H_{ax}), 1.99 (s, 6 H, 2 × O_2CCH_3), 2.02 (s, 6 H, 2 × O_2CCH_3), 2.15 (s, 3 H, 3-O_2CCH_3), **2.52 (dt, J_{gem} = 12.5 Hz, $J_{6\text{-Heq},1}$ = $J_{6\text{-Heq},5}$ = 5.1 Hz, 1 H, 6-H_{eq})**, 5.03 (dd, $J_{2,1}$ = 10.2 Hz, $J_{2,3}$ = 2.9 Hz, 2 H, 2-H and 4-H), 5.24 (ddd, $J_{1,6\text{-Hax}}$ = 11.7 Hz, $J_{1,2}$ = 10.2 Hz, $J_{1,6\text{-Heq}}$ = 5.1 Hz, 2 H, 1-H and 5-H), **5.59 (t, $J_{3,2}$ = $J_{3,4}$ = 2.9 Hz, 1 H, 3-H) ppm**.

NMR Data of Pentaacetate 37 (Figure 6)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3 H, O_2CCH_3), 2.00 (s, 3 H, O_2CCH_3), 2.01 (s, 3 H, O_2CCH_3), 2.03 (s, 3 H, O_2CCH_3), 2.04 (ddd, $J_{6\text{-Hax},1}$ = 12.5 Hz, J_{gem} = 12.1 Hz, $J_{6\text{-Hax},5}$ = 11.9 Hz, 1 H, 6-H_{ax}), 2.17 (s, 3 H, O_2CCH_3), 2.22 (dddd, J_{gem} = 12.1 Hz, $J_{6\text{-Heq},5}$ = 5.2 Hz, $J_{6\text{-Heq},1}$ = 4.7 Hz, $^4J_{6\text{-Heq},2}$ = 1.3 Hz, 1 H, 6-H_{ax}), 4.95 (ddd, $J_{5,6\text{-Hax}}$ = 11.9 Hz, $J_{5,4}$ = 9.7 Hz, $J_{5,6\text{-Heq}}$ = 5.2 Hz, 1 H, 5-H), 4.97 (dd, $J_{3,4}$ = 10.5 Hz, $J_{3,2}$ = 2.8 Hz, 1 H, 3-H), 4.98 (ddd, $J_{1,6\text{-Hax}}$ = 12.5 Hz, $J_{1,6\text{-Heq}}$ = 4.7 Hz, $J_{1,2}$ = 2.6 Hz, 1 H, 1-H), **5.40 (dd, $J_{4,3}$ = 10.5 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 5.55 (ddd, $J_{2,3}$ = 2.8 Hz, $J_{2,1}$ = 2.6 Hz, $^4J_{2,6\text{-Heq}}$ = 1.3 Hz, 1 H, 2-H) ppm**.

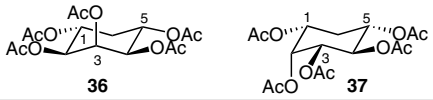


Figure 6

(47) The authors of ref. 8b peracetylated the mixture of glycols *ent*-**39** and *ent*-**40** (mentioned in ref. 44) to obtain the pentaacetates (*meso*)-**36** and *ent*-**37**. They separated the latter compounds by flash chromatography on silica gel, which we could not.

(48) Complementary diastereocontrol of cyclohexene dihydroxylations due to the presence of DHQ- vs. DHQD-substituted ligands: (a) Chida, N.; Ohtsuka, M.; Nakazawa, K.; Ogawa, S. *J. Org. Chem.* **1991**, *56*, 2976. (b) Mahapatra, T.; Nanda, S. *Tetrahedron: Asymmetry* **2010**, *21*, 2199.

(49) According to ref. 8b, an ammonolysis of the pentaacetate (*meso*)-**36** (mentioned in ref. 47) rendered the quercitol **8e**. Likewise, an ammonolysis of the pentaacetate *ent*-**37** (also mentioned in ref. 47) gave the quercitol *ent*-**8f**. Both quercitols were diastereomerically pure.

(50) **NMR Data of *neo*-Quercitol (8e, Figure 7)**

^{1}H NMR (500 MHz, D_2O): δ = 1.32 (dt, J_{gem} = 12.3 Hz, $J_{6\text{-Hax},1}$ = $J_{6\text{-Hax},5}$ = 11.8 Hz, 1 H, 6-H_{ax}), 2.18 (dt, J_{gem} = 12.3 Hz, $J_{6\text{-Heq},1}$ = $J_{6\text{-Heq},5}$ = 4.8 Hz, 1 H, 6-H_{eq}), 3.44 (dd, $J_{2,1}$ = 9.7 Hz, $J_{2,3}$ = 3.0 Hz, 2 H, 2-H and 4-H), 3.79 (ddd, $J_{1,6\text{-Hax}}$ = 11.8 Hz, $J_{1,2}$ = 9.7 Hz, $J_{1,6\text{-Heq}}$ = 4.8 Hz, 2 H, 1-H and 5-H), 4.03 (t, $J_{3,2}$ = $J_{3,4}$ = 3.0 Hz, 1 H, 3-H) ppm.

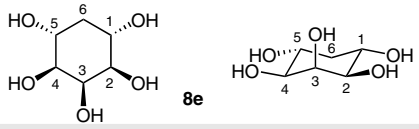


Figure 7

(51) **NMR Data of (–)-*epi*-Quercitol (8f, Figure 8)**

^{1}H NMR (400 MHz, D_2O): δ = 1.74 (m_c, *1H*, 6-H_{ax}), 1.96 (m_c, 1 H, 6-H_{eq}), 3.67 - 3.54 (m, 3 H, 3-H, 4-H, 5-H), 3.77 (ddd, $J_{1,6\text{-Hax}}$ = 12.3 Hz, $J_{1,6\text{-Heq}}$ = 4.5 Hz, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H), 3.98 (m_c, 1 H, 2-H) ppm.

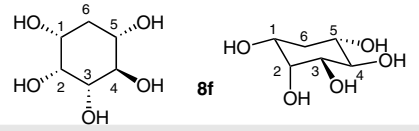


Figure 8

(52) We reached five quercitols of the present study via a total of four diastereoisomeric cyclohexenetriol triacetate precursors: **20** [Scheme 4; → (–)-*proto*-quercitol (**8b**)], **30** [Scheme 5; → (+)-*talo*-quercitol (**8c**)], **32** [Scheme 6; → (–)-*gala*-quercitol (**8d**)], and **38** [Scheme 7; → *neo*-quercitol (**8e**) and (–)-*epi*-quercitol (**8f**)]. The value of the eight stereoisomeric cyclohexenetriol triacetates as precursors of synthetic cyclohexitols was recognized previously by Balci et al.[22] and by: Kee, A.; O'Brien, P.; Pilgram, C. D.; Watson, S. T. *Chem. Commun.* **2000**, 1521.