# A Concise and Convenient Synthesis of DL-*proto*-Quercitol and DL-*gala*-Quercitol *via* Ene Reaction of Singlet Oxygen Combined with [2 + 4] Cycloaddition to Cyclohexadiene†

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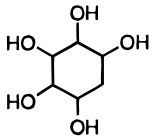
*Received November 8, 1996*⊗

Photooxygenation of 1,4-cyclohexadiene afforded hydroperoxy endoperoxides **3** and **4** in a ratio of 88:12. Reduction of **3** with $LiAlH_4$ or thiourea followed by acetylation of the hydroxyl group and $KMnO_4$ oxidation of the double bond gave *proto*-quercitol **10b**. Application of the same reaction sequences to **4** resulted in the formation of *gala*-quercitol **14**. Quercitols were easily obtained by ammonolysis of acetate derivatives in MeOH. The outcome of dihydroxylation reactions were supported by conformational analysis.

Stereospecific [4 + 2] Diels−Alder addition of singlet oxygen to cyclic dienes followed by opening of the resulting peroxide linkage by appropriate reducting reagents is a reaction which has as yet no equivalent in the synthetic methodology to form cyclic 1,4-dihydroxyl compounds in a cis configuration. Recently, we have applied this methodology to the stereospecific synthesis of the highly hydroxylated cyclohexane derivatives[1] and synthesized conduritols and their derivatives[2] in a short and stereospecific way. Parallel to the execution of efficient design of conduritol derivatives we embarked on a general synthetic approach to cyclopentols. For this reason we applied for the first time singlet oxygen ene reaction combined with the singlet oxygen [2 + 4] addition successfully to the synthesis of *proto*-quercitol.[3]




**Quercitol**

Quercitol has been used as a generic term for cyclohexanepentols. The family of quercitols is one of the largest all-known family of diastereoisomers in organic chemistry.[4] Cyclohexanepentols can exist in 16 stereoisomeric forms, of which four are symmetric, the 12 others being grouped in six pairs of optical mirror images. Only three optically active forms have been found in nature and only in plants.[5]

So far, 10 possible diastereoisomers of quercitols have been synthesized by different methods.[2d] The synthesis of *proto*-quercitol was accomplished by McCasland[4b] using (−)-*chiro*-inositol, by Suami[6a] using DL-1,2-anhydro-5,6-*O*-cyclohexylidene-*chiro*-inositol, and by Cambie[6b] using conduritol-A. In all previously reported syntheses, starting materials have been natural products or compounds which required many steps to synthesize. Herewith, we describe a concise and convenient three step synthesis of *proto*- and *gala*-quercitols starting from cyclohexadiene.

In our previous study, we successively used 1,3-cyclohexadiene for stereospecific synthesis of conduritol-A[1c] and conduritol-F.[1d,e] In our synthesis, 1,4-oxygen functional groups were incorporated to cyclohexane ring by singlet oxygen. Besides these, transformations using singlet oxygen for synthesis of cyclitol derivatives have been described.[7,8]

## Results and Discussion

Tetraphenylporphyrin-sensitized photooxygenation of 1,4-cyclohexadiene in methylene chloride at room temperature resulted in the formation of the bicyclic endoperoxides **3** and **4** in a ratio of 88:12 (Scheme 1). The

† Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday.

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⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1997.

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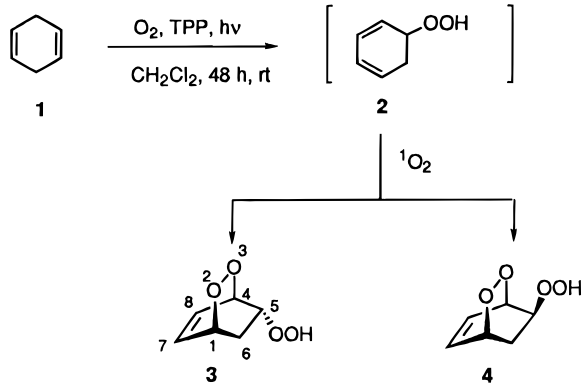
S0022-3263(96)02092-0 CCC: $14.00 

**Scheme 1**




reaction mixture was chromatographed on silica gel column with ether/petroleum ether (1:1) as eluant.

The structures of **3** and **4** were assigned by $^1$H and $^{13}$C NMR. The most conspicuous features in the $^1$H NMR spectra of the endoperoxides **3** and **4** are two distinct AB systems which correspond to two olefinic and two methylenic protons. Olefinic protons of **3** resonating at $\delta$ 6.56−6.73 show further splitting with adjacent bridgehead protons. Methylenic protons resonate as an AB system $\delta$ 2.54 and 1.20 and gave most useful information for the structure of these endoperoxides. The B part of the AB system (low field resonance, $H_{6exo}$) is split into a doublet of doublets of doublets ($J$ = 14.2, 8.1, and 3.7 Hz). The large splitting originates from the geminal coupling where the second doublet splitting (8.21 Hz) arises from the vicinal hydrogen which is attached to the $C_5$ carbon atom. The high-field part of the AB system resonates as triplets of doublet. The coupling constant between $H_{6endo}$ and bridgehead proton is $J$ = 2.3 Hz. Bridgehead proton $H_1$ has a larger coupling to $H_{6exo}$ proton than to $H_{6endo}$ proton. Geometry optimization calculations (AM1) show a dihedral angle of 71° for $H_1-H_{6endo}$ and 48.5° for $H_1-H_{6exo}$, which is consistent with our assignments. Unequivocal assignment of these methylene signals permitted identification of $H_4$ ($\delta$ 5.08), $H_8$ ($\delta$ 6.56), $H_7$ ($\delta$ 6.73), $H_1$ ($\delta$ 4.58), and $H_5$ ($\delta$ 4.50) by observation of the diagonal cross peaks between appropriate protons in the COSY spectrum. The relative stereochemistry of the hydroxy peroxide group at $C_5$ was determined from the coupling constants between protons $H_4$ and $H_5$. The assignments for the syn isomer **4** were based on a series of homonuclear decoupling experiments. $^{13}$C NMR spectral data are also in agreement with the proposed structures.

For the mechanism of formation of these interesting endoperoxides containing hydroperoxide groups, we assume that 1,4-cyclohexadiene first undergoes an ene reaction[8a,b] with the double-activated methylene groups to give the hydroperoxide **2**. Because of the unfavorable arrangement of double bonds, a [2 + 4] cycloaddition can be excluded. On the other hand, formation of dioxetane by addition of singlet oxygen to one of these double bonds can occur only with certain activated double bonds.[8a] Addition of singlet oxygen to a diene[9] unit results in the formation of the isolated products **3** and **4**. Since the hydroperoxide **2** has no plane of symmetry, singlet oxygen approaches the diene unit in **2** preferentially from the sterically less crowded face of the molecule. All efforts

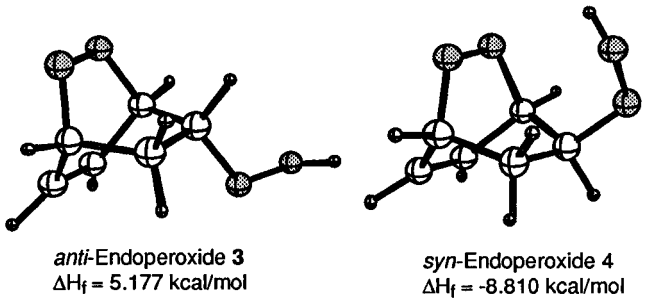


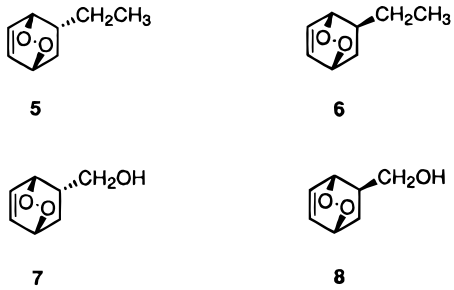

**Figure 1.** Optimized geometries for isomers **3** and **4**.

**Table 1. Results from AM1 Calculations**

| substrate | $\Delta H_f$ (kcal/mol) | dipole moments (Debye) |
|---|---|---|
| **3** | −5.177 | 2.48 |
| **4** | −8.810 | 3.45 |
| **5** | −1.147 | 3.18 |
| **6** | −1.241 | 2.99 |
| **7** | −40.32 | 1.65 |
| **8** | −42.45 | 3.71 |

to isolate any trace of **2** were unsuccessful. We believe that the rate of addition of singlet oxygen to the diene system **2** is much faster than the rate of the ene reaction. In order to rationalize the formation of these isomers, we have carried out some AM1 calculations.[10]

The optimized geometrys of these isomers **3** and **4** (Figure 1) were calculated using the AM1 method. Results from AM1 calculations show that the minor isomer **4** has a lower heat of formation (−8.810 kcal/mol) than the major isomer (−5.177 kcal/mol) which indicates that the minor isomer is thermodynamically the most stable one (Table 1). This can be rationalized by the existence of a hydrogen-bonding interaction between hydroperoxide hydrogen and peroxide linkage, which can also be seen from the short distance (2.1 Å). For comparison, we have calculated the heats of formation of the corresponding ethyl and hydroxymethyl derivatives **5**−**8**. Ethyl derivatives **5** and **6** show similar heats of




formation as they have no hydrogen bonding to the peroxide linkage. On the other hand, hydroxymethyl derivatives **7** and **8** show an energy difference of $\Delta H_F$ = 2 kcal/mol where syn isomer **8** is energetically favored, as expected. These results support the stabilization of the exo isomer **4** by the hydrogen bond interactions. The fact that the kinetically controlled product is formed as the major product indicates the steric factors in the transition state determine the course of the cycloaddition reaction of singlet oxygen to the diene unit.

After successful isolation and characterization of endoperoxides **3** and **4**, we turned our attention to the reduction of both peroxide linkages in **3** and **4**. The

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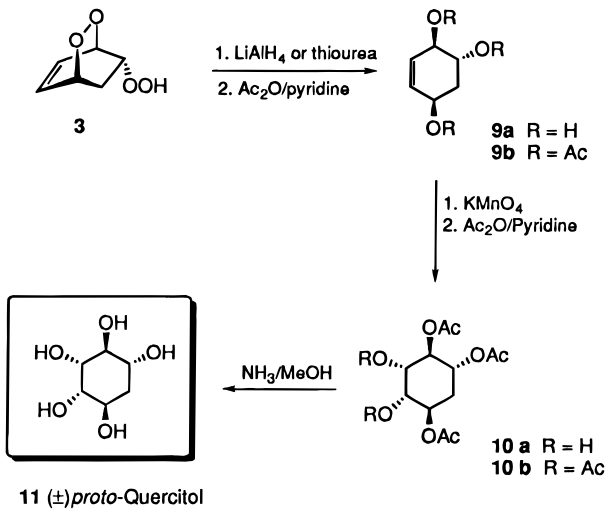
**Scheme 2**




peroxide linkage is highly susceptible to reductive cleavage by a variety of reductants.[11] Bicyclic endoperoxides can be readily reduced by catalytic hydrogenation to the corresponding *cis*-diols. Under the conditions for forming *cis*-diols, any double bonds present are also reduced. Selective reduction of both peroxide linkages in **3** was performed with either thiourea or $LiAlH_4$ under very mild conditions to give the cyclohexenetriol **9a** (Scheme 2). Since only the oxygen−oxygen bonds break in this reaction, it preserves the configuration at all three carbon atoms. For further structural proof, **9a** was converted to the corresponding acetate **9b** which has been fully characterized from the spectroscopic data.

Cyclohexenetriacetate **9b** is an ideal substrate for the synthesis of quercitols and aminoquercitols. By comparison of the configuration of this triacetate with the configuration of *proto*-quercitol, it can easily be seen that the three hydroxyl groups have been incorporated in the six-membered ring correctly as desired for the synthesis of *proto*-quercitol. In the next step, the double bond has to be oxidized in a cis fashion. The oxidation of olefins with permanganate is not commonly used as a preparative method because of its typically low selectivity.[12] However, we chose to examine the oxidation of triacetate **9b** with permanganate with the intention of introducing the two hydroxyl groups in a cis configuration to the double bond to complete the synthesis of *proto*-quercitol. Treatment of **9b** with $KMnO_4$ (−15 °C, $H_2O$) gave to our surprise only one diol **10a** in an isolated yield of 66%. Careful NMR studies did not reveal the formation of any trace of the other diastereoisomer. For characterization of the product, we converted **10a** to DL-*proto*-quercitol pentaacetate **10b**.[13] Deacetylation of **10b** with ammonia in methanol afforded DL-*proto*-quercitol **11** in quantitative yield. The spectral data of **10b** and **11** were identical with those reported in the literature.[14]

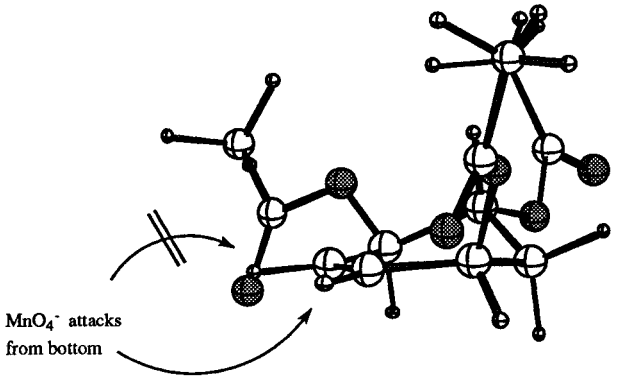
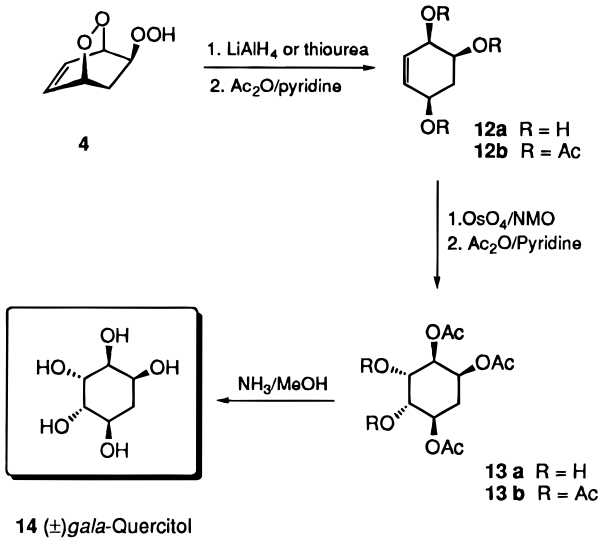



**Figure 2.** Lowest energy conformation of **9b**.

**Scheme 3**




In order to explain the formation of one isomer during $KMnO_4$ oxidation, we have carried out conformational analysis using the AM1 method on the triacetate **9b**. This analysis indicates clearly that anti attack to the double bond should be favored since acetoxyl groups bonded to C1 and C2 are sterically more demanding and block the syn face of the molecule (Figure 2).

The same methodology was applied to the synthesis of *gala*-quercitol **14** starting from the minor isomer **4** (Scheme 3). Successful reduction of peroxide linkages in **4** followed by acetylation of formed triol **12a** using acetic anhydride−pyridine resulted in the formation of the corresponding triacetate **12b**. For cis hydroxylation of the double bond in **12b**, an $OsO_4$−NMO oxidation[15] method was applied. Thus, the formed triacetoxy diol **13a** was converted to the acetate derivative[13b] **13b** for further characterization.

*gala*-Quercitol **14** itself was readily and quantitatively obtained by ammonolysis of *gala*-quercitol pentaacetate **13b**, which was characterized by comparison of its physical data with those reported[13,16] in the literature.

In summary, with relatively little synthetic effort we have achieved the stereospecific synthesis of DL-*proto*-quercitol and DL-*gala*-quercitol in three steps starting from commercially available 1,4-cyclohexadiene and introduced the complex stereochemistry in a very simple

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way. Further studies of the chemistry of the double bond in **9** and **13** directed toward the synthesis of other quercitols and aminoquercitols are currently in progress.

## Experimental Part

**General.** Melting points were determined on a melting apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from KBr pellets on an infrared recording spectrophotometer. $^1$H-NMR spectra were recorded on 60, 200, and 400 MHz spectrometer and are reported in $\delta$ units with $SiMe_4$ as internal standard. All column chromatography was performed on silica gel (60 mesh).

**Photooxygenation of 1,4-Cyclohexadiene.** To a stirred solution of 1,4-cyclohexadiene (1.0 g, 12.5 mmol) in 100 mL of $CH_2Cl_2$ was added 20 mg of tetraphenylporphyrin (TPP). The resulting mixture was irradiated with a projection lamp (150 W) while oxygen was being passed through solution and the mixture was stirred for 48 h at room temperature. The $^1$H-NMR spectrum of the mixture showed that the ratio of **3:4** was 88:12. Evaporation of the solvent (30 °C, 20 mmHg) and chromatography of the residue on a silica gel column (100 g) eluting with hexane/ether (1:1) gave as the first fraction endoperoxide **3** (1.15 g, 63%) and as the second fraction endoperoxide **4** (0.12 g, 7%).

***anti*-2,3-Dioxabicyclo[2.2.2]oct-7-en-5-yl hydroperoxide (3)**: colorless solid; mp 131−132 °C from $CHCl_3$/ether; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 8.85 (br s, 1H), 6.73 (ddd, $J$ = 8.3, 6.3, 1.8 Hz, 1H), 6.56 (ddd, $J$ = 8.3, 6.9, 1.4 Hz, 1H), 5.08 (m, 1H), 4.69 (m, 1H), 4.60 (ddd, $J$ = 8.1, 4.0, 2.5 Hz, 1H), 2.54 (ddd, $J$ = 14.2, 8.1, 3.7 Hz, 1H), 1.20 (dm, $J$ = 14.2, 1H); $^{13}$C-NMR (50 MHz, $CDCl_3$) $\delta$ 29.8, 71.1, 71.3, 75.2, 129.5, 134.3; IR (KBr) 3380, 2920, 1280, 1210. Anal. Calcd for $C_6H_8O_4$: C, 50.01; H, 5.59. Found: C, 49.45; H, 5.34.

***syn*-2,3-Dioxabicyclo[2.2.2]oct-7-en-5-yl hydroperoxide (4)**: colorless solid; mp 98−100 °C, from $CHCl_3$/petroleum ether; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 8.82 (br s, 1H), 6.74 (ddd, $J$ = 8.2, 5.8, 1.7 Hz, 1H), 6.63 (ddd, $J$ = 8.2, 6.2, 1.8 Hz, 1H), 5.06 (dq, $J$ = 6.2, 1.7 Hz, 1H), 4.64 (m, 1H), 4.21 (ddd, $J$ = 9.9, 4.3, 1.9 Hz, 1H), 1.96 (ddd, $J$ = 14.3, 9.9, 2.4 Hz, 1H), 1.83 (dt, $J$ = 14.3, 4.0 Hz, 1H); $^{13}$C-NMR (50 MHz, $CDCl_3$) $\delta$ 27.4, 70.9, 72.5, 77.6, 130.1, 135.1; IR (KBr) 3230, 2980, 1446, 1370. Anal. Calcd for $C_6H_8O_4$: C, 50.01; H, 5.59. Found: C, 49.35; H, 5.26.

**(2,5/1)-Cyclohex-3-enetriol (9a). (a) By reduction of 3 with $LiAlH_4$.** To a magnetically stirred slurry of 261 mg (6.87 mmol) of $LiAlH_4$ in 50 mL of THF was added a solution of 450 mg (3.13 mmol) of endoperoxide **3** in 25 mL of THF at 0 °C under nitrogen, during 3 h. The reaction mixture was stirred at rt for 1 h, and 20 g of silica gel was added. After 12 h of stirring at rt, 50 mL of methanol was added and the solution was filtered. The solvents were rotoevaporated (at 40 °C, 20 mmHg), and the residue was purified by column chromatography (35 g of basic alumina), eluting with $CHCl_3$/methanol (95:5), affording pure (2,5/1)-cyclohex-3-enetriol **9a** (163 mg, 40%).

**(b) By reduction of 3 with Thiourea.** To a magnetically stirred slurry of 1.06 g (13.88 mmol) of thiourea in 25 mL of methanol was added a solution of 1.00 g (6.94 mmol) of endoperoxide **3** in 50 mL of methanol at 25 °C. After completion of addition (ca. 10 min), the mixture was stirred for 1 h, the solids were removed by filtration, methanol was rotoevaporated (at 35 °C, 20 mmHg), and the residue was purified by column chromatography on silica gel (100 g) elution with $CHCl_3$/methanol (97:3) and afforded the pure (2,5/1)-cyclohex-3-enetriol **9a** (630 mg, 70%): colorless solid; mp 76−78 °C from absolute methanol; $^1$H-NMR (200 MHz, $D_2O$) $\delta$ 5.75 (br d, $J$ = 10.5 Hz, 1H), 5.66 (dd, $J$ = 10.5, 1.8 Hz, 1H), 4.28 (br q, $J$ = 3.8 Hz, 1H), 3.91 (ddd, $J$ = 7.2, 1.7, 1.4 Hz, 1H), 3.73 (ddd, $J$ = 11.9, 7.2, 4.7 Hz, 1H), 1.82 (m, 2H); $^{13}$C-NMR (50 MHz, $D_2O$) $\delta$ 38.7, 67.1, 71.4, 74.3. 132.3, 133.8; IR (KBr) 3350, 2920, 1440, 1190. Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.01; H, 6.71.

**(1,2,5)-Cyclohex-3-enetriol (12a).** Reduction of **4** with $LiAlH_4$ and with thiourea was carried out as described above: yield 55% from $LiAlH_4$ reaction, 50% from thiourea reaction; colorless solid; mp 95−96 °C from ethanol; $^1$H-NMR (200 MHz, $D_2O$) $\delta$ 5.76 (br s, 2H), 4.21 (dd, $J$ = 9.7, 6.1 Hz, 1H), 4.0 (m, 1H), 3.61 (dt, $J$ = 12.2, 3.7 Hz, 1H), 1.96 (m, 1H), 1.56 (dt, $J$ = 14.1, 12.2, 9.7 Hz, 1H); $^{13}$C-NMR (50 MHz, $D_2O$) $\delta$ 37.8, 69.6, 70.8, 71.3, 131.6, 138.9; IR (KBr) 3390, 2950, 1472, 1270. Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.67; H, 6.62.

**(2,5/1)-Triacetoxy-3-cyclohexene (9b).** To a magnetically stirred solution of triol **9a** (400 mg, 3.07 mmol) in 5 mL of pyridine was added $Ac_2O$ (1.25 g, 12.25 mmol). The reaction mixture was stirred at rt for 6 h. The mixture was cooled to 0 °C and 200 mL of 1 N HCl solution added, and the mixture was extracted with ether (3 × 100 mL). The combined organic extracts were washed with $NaHCO_3$ solution (25 mL) and water (10 mL) and then dried ($Na_2SO_4$). Removing of the solvent under reduced pressure and recrystallization of product from ethyl acetate/*n*-hexane gave **9b** (525 mg, 67%, colorless solid, mp 30−31 °C): $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 5.89 (br dd, $J$ = 10.0, 2.9 Hz, 1H), 5.75 (dd, $J$ = 10.0, 2.5 Hz, 1H), 5.31 (m, 2H), 5.17 (ddd, $J$ = 11.1, 6.9, 4.4 Hz, 1H), 2.20−1.90 (m, 10H); $^{13}$C-NMR (50 MHz, $CDCl_3$) $\delta$ 21.4, 21.5, 21.6, 31.5, 66.7, 69.1, 70.6, 129.2, 129.4, 170.6, 170.8, 170.9; IR (KBr) 2940, 1740, 1430. Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 55.93; H, 6.52.

**(1,2,5)-Triacetoxy-3-cyclohexene (12b).** The same procedure was applied as described above: yield 50%; colorless solid; mp 92−93 °C from chloroform/*n*-hexane; $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 5.90 (AB system, $J$ = 10.1, 2.8, 1.4 Hz, 2H), 5.40 (m, 2H), 5.01 (dt, $J$ = 10.6, 3.9 Hz, 1H), 2.20−1.90 (m, 10H); $^{13}$C-NMR (50 MHz, $CDCl_3$) $\delta$ 21.3, 21.4, 21.5, 29.3, 65.8, 67.2, 68.0, 126.5, 132.6, 170.4, 170.6, 170.8; IR (KBr) 3004, 1778, 1395. Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.25; H, 6.29. Found: C, 56.63; H, 6.41.

**DL-*proto*-Quercitol Pentaacetate (10b).** To a magnetically stirred ethanol solution (100 mL) of triacetate **9b** (4.0 g, 15.63 mmol) was added a solution of $KMnO_4$ (2.46 g, 15.63 mmol) and $MgSO_4$ (1.87 g, 15.63 mmol) in water (40 mL) at −5 °C for 7 h. After the addition was complete, the reaction mixture was stirred for additional 15 h at the given temperature and then filtered. The precipitate was washed several times with hot water. The combined filtrates were concentrated to 20 mL by rotoevaporation. The aqueous solution was extracted with ethyl acetate (3 × 30 mL), and the extracts were dried ($Na_2SO_4$). Evaporation of the solvent gave triacetoxy diol **10a** (3.00 g, 66%), which was submitted to acetylation as described above: 2.81 g, 73%; colorless solid; mp 115−116 °C (lit.[9,13a] mp 114−116.5 °C, lit.[13b] mp 124−125 °C) from ethyl acetate/*n*-hexane; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 5.37 (t, $J$ = 10.0 Hz, 1H), 5.33 (dd, $J$ = 4.0, 3.2 Hz, 1H), 5.23 (dd, $J$ = 10.0, 3.2 Hz, 1H), 5.16 (ddd, $J$ = 14.4, 9.2, 5.2 Hz, 1H), 5.08 (br q, $J$ = 3.6 Hz, 1H); 2.23 (br dt, $J$ = 14.4, 5.2, 3.6 Hz, 1H), 2.14 (br s, 6H), 2.04 (br s, 6H), 2.00 (m, 1H), 2.00 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 20.5, 20.6, 20.7, 20.8, 20.8, 29.7, 67.4, 68.2, 68.8, 69.3, 70.7, 169.1, 169.7, 169.8, 169.9; IR (KBr) 2960, 1740, 1440.

**DL-*proto*-Quercitol (11).** Pentaacetoxycyclohexane (**10b**) (300 mg, 0.802 mmol) was dissolved in 15 mL of absolute methanol. While dry $NH_3$ was passed through solution, the mixture was stirred for 2 h at room temperature. Evaporation of methanol and formed acetamide gave *proto*-quercitol **11** in nearly quantitative yield (132 mg): mp 228−229 °C (lit. mp 227 °C,[14b] 228−230 °C,[13b] 237 °C[6]) from absolute EtOH; $^1$H-NMR (200 MHz, $D_2O$) $\delta$ 3.94 (br q, $J$ = 3.3 Hz, 1H), 3.83 (dd, $J$ = 3.3, 3.5 Hz, 1H), 3.70 (ddd, $J$ = 11.4, 9.3, 5.1 Hz, 1H), 3.62 (dd, $J$ = 9.6, 3.3 Hz, 1H), 3.47 (t, $J$ = 9.3, 9.6 Hz, 1H), 1.89 (br ddd, $J$ = 14.0, 5.1, 3.9 Hz, 1H), 1.72 (ddd, $J$ = 14.0, 11.4, 2.9 Hz, 1H); $^{13}$C-NMR (50 MHz, $D_2O$) $\delta$ 36.2, 71.5, 71.8, 73.9, 75.2, 77.5; IR (KBr) 3300, 2900, 1420.

***gala*-Quercitol Pentaacetate (13b).** A 50 mL three-necked, round-bottomed flask, equipped with a magnetic stirrer and a nitrogen inlet, was charged with 91 mg (0.67 mmol) of NMO, 1 mL of water, and 0.5 mL of acetone. To this solution were added ca. 2.0 mg of $OsO_4$ (0.008 mmol) and 170 mg (0.66 mmol) of triacetate **11b**. The resulting mixture was stirred vigorously under nitrogen at rt. During the overnight stirring, the reaction mixture became homogeneous.

After 24 h, the reaction was complete. Sodium hydrosulfite (0.01g) and 0.5 g of Florisil slurried in 2 mL of water were added, the slurry was stirred for 10 min, and the mixture was filtered through a pad of 0.5 g of Celite in a 50 mL sintered-glass funnel. The Celite cake was washed with acetone (3 × 10 mL). The filtrate was neutralized to pH 7 with $H_2SO_4$. The organic layer was removed *in vacuo*. The pH of the resulting aqueous solution was adjusted to pH 5 with sulfuric acid, and the triacetoxy diol **13a** was separated from *N*-methylmorpholine hydrosulfate by extraction with ethyl acetate (4 × 20 mL). The combined ethyl acetate extracts were washed with 2 mL of 25% NaCl solution and two or three times with water and dried ($Na_2SO_4$). Evaporation of solvent gave 134 mg of triacetoxy diol (70%). The same procedure as described above was applied for acetylation of triacetoxy diol **13a** (110 mg, 64%, mp 116−117 °C (lit. mp 117−118 °C,[13b] 92 °C[15]) recrystallized from absolute 2-propanol): $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 5.39 (m, 1H), 5.26 (m, 3H), 5.11 (dt, $J$ = 8.83, 4.42 Hz, 1H), 1.98−2.27 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.01(s, 3H), 2.00 (s, 3H); $^{13}$C-NMR (50 MHz, $CDCl_3$) $\delta$ 22.7, 22.8, 22.9, 31.19, 68.79, 69.7, 70.2, 71.8, 171.3, 171.3, 171.7; IR (KBr) 3055, 2980, 1753, 1446.

**DL-*gala*-Quercitol (14).** **14** was synthesized by ammonolysis of **13b** (90 mg, 0.24 mmol) as described above by the synthesis of *proto*-quercitol **11** in almost quantitative yield (39 mg, 0.24 mmol): mp[13] 256−257 °C recrystallized from absolute methanol; $^1$H-NMR (200 MHz, $D_2O$) $\delta$ 4.66 (m, 1H), 4.02 (m, 2H), 3.76 (dd, $J$ = 10.2, 4.4 Hz, 1H), 3.66 (dd, $J$ = 9.1, 3.3 Hz, 1H), 2.07 (m, 1H), 1.72 (dt, $J$ = 11.4, 10.8 Hz, 1H); $^{13}$C-NMR (50 MHz, $D_2O$) $\delta$ 38.0, 71.0, 72.5, 76.2, 76.5, 76.8; IR (KBr) 3410, 2950, 1676, 1421.

**Acknowledgment.** The authors are indebted to the Department of Chemistry (Atatürk University) and the TBAG-DPT-6 for financial support of this work and State Planning Organization of Turkey (DPT) for purchasing a 200 MHz NMR spectrometer. M.B. thanks to Fulbright Scholarship Board for a grant and Professor Philip Shevlin for helpful discussions during the preparation of the manuscript.

JO962092+