Notes

A Convenient Synthesis of (±)-*talo*-Quercitol (1-Deoxy-*neo*-Inositol) and (±)-*vibo*-Quercitol (1-Deoxy-*myo*-Inositol) *via* Ene Reaction of Singlet Oxygen

Ahmet Maraş,[†] Hasan Seçen,[†] Yaşar Sütbeyaz,*[,†] and Metin Balcı*[,‡]

Department of Chemistry, Faculty of Arts and Sciences, Atatürk University, 25240 Erzurum, Turkey, and Department of Chemistry, Faculty of Arts and Sciences, Middle East Technical University, 06531 Ankara, Turkey

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The polyhydroxy cyclohexanes have been an interest to those concerned with carbohydrates[1] . The first known cyclohexanepentol was a dextrorotatory cyclitol obtained from the acorns of *Quercus* species (oaks)[2] , hence the name (+)-*proto*-quercitol. "Quercitol" has been used as a generic term for cyclohexanepentols. Ten diastereoisomers are predicted for the quercitols. All 10 are known and only the (+)-*proto*,[2] (−)-*proto*,[3] and (−)-*vibo*[4] stereoisomers have been found in nature. Methods which have been used for quercitol synthesis include reduction (hydrogenation) of inososes, inosos oximes, or deoxyinososes; hydrogenation of bromoquercitols; reduction of anhydroinositols; and transformation of conduritols.[5] Meanwhile, synthesis of *talo*-quercitol and *vibo*-quercitol was described by McCasland[6] and Nakajima[7] starting from haloinositols and conduritol-E, respectively. In all previously reported syntheses, starting materials have been natural products or compounds which required many steps to synthesize. Recently we described a simple route leading to the synthesis of quercitols where we applied for the first time a singlet oxygen ene reaction combined with the singlet oxygen [2 + 4] addition[8] successively to the synthesis of *proto*-quercitol[9,10] and *gala*-quercitol.[10] Here with we describe a short and efficient synthesis of (±)-*talo*-quercitol and (±)-*vibo*-quercitol starting from commercial 1,3-cyclohexadiene where we used again ene reaction of singlet oxygen.[11]

Results and Discussion

1,4-Cyclohexadiene **1** was used as the starting material for the synthesis of *talo*-quercitol. OsO_4-catalyzed NMO oxidation[12] of **1** afforded diol **2**. The resulting *cis*-diol **2** was protected by ketal formation with 1,2-dimethoxypropane. Tetraphenylporphyrin-sensitized photooxygenation of ketal **3** in methylene chloride at room temperature gave the hydroperoxide **4** in high yield, via ene reaction of singlet oxygen, as the sole product (Scheme 1). The peroxide linkage is highly susceptible to reductive cleavage by a variety of reductants.[13] Selective reduction of peroxide linkage was performed with thiourea under very mild conditions to give the alcohol **5a**. Since the only oxygen−oxygen bond breaks in this reaction, it preserves the configuration at the peroxide-bonded carbon atom. For further structural proof, **5a** was converted to the corresponding acetate **5b** which has been fully characterized on the basis of the spectroscopic data.

Proton and carbon NMR studies of **5b** indicated the formation of an unsymmetrical compound as expected. The proton adjacent to the acetoxy group appears as a multiplet at 5.28 ppm, the alkoxy protons at 4.32 ppm as a multiplet, and the methylene protons appear as an AB system at 2.31 and 1.65 ppm. An 11-line ^{13}C NMR spectrum is also in agreement with the proposed constitution. However, on the basis of NMR data alone we were not able to assign the correct configuration of the acetoxy group. The configuration of the acetoxyl group was confirmed by observation of NOE effects. Irradiation at the resonance signals of alkoxy protons at $\delta = 4.32$ caused signal enhancement at the resonances of the adjacent double bond proton, methylenic protons, and especially the methyl resonance (acetyl group) at $\delta =$ 1.92. These observations clearly indicate the anti-configuration of acetoxyl group in **5b**. Singlet oxygen is quite sensitive to steric consideration and approaches the substrate predominantly, if not exclusively, from the less congested side.[14] The pronounced stereoselectivity of this

[†] Atatürk University
[‡] Middle East Technical University

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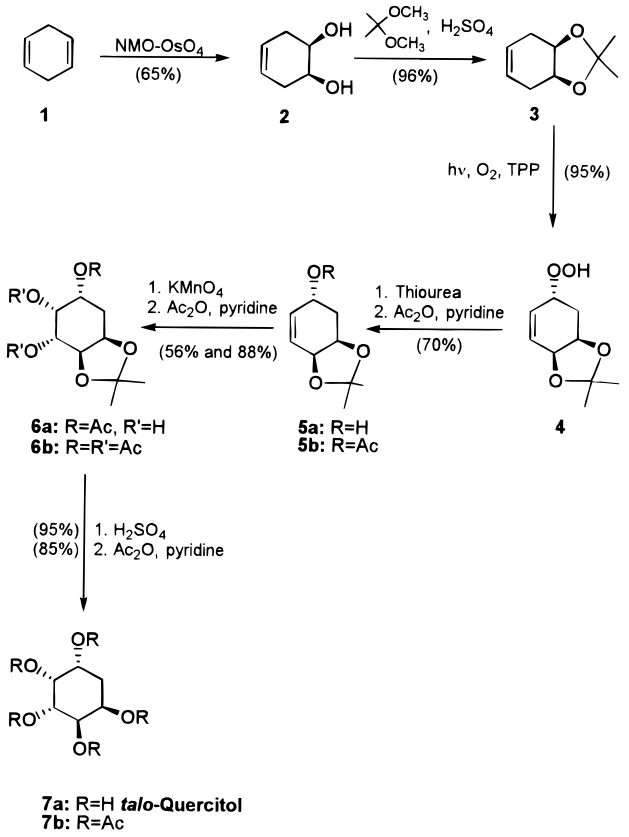
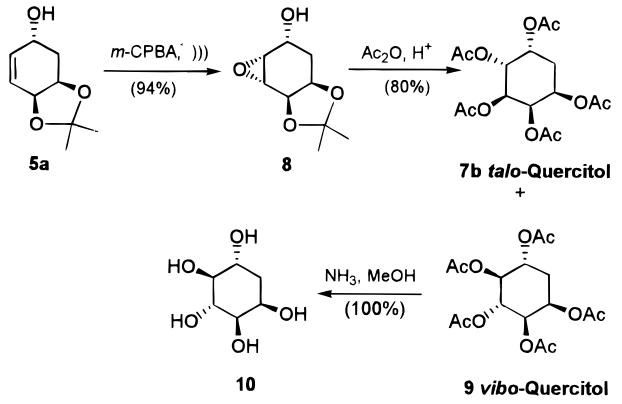
Scheme 1



ene reaction is rationalized by the strong steric effect between the incoming singlet oxygen and bulky methyl groups. 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. However, we chose to examine the oxidation of acetate **5b** with permanganate with the intention of introducing the two hydroxyl groups in a cis configuration to the double bond to complete the synthesis of *talo*-quercitol. Treatment of **5b** with $KMnO_4$ (−5 °C) gave to our surprise only one diol **6a** in an isolated yield of 56%. Careful NMR studies did not reveal the formation of any trace of the other diastereomer. For characterization of the product, **6a** was converted to the corresponding triacetate **6b,** which upon hydrolysis gave *talo*-quercitol **7a** (Scheme 1). For further characterization of **7a** we prepared the corresponding pentaacetate in 85% yield. The spectral data of **7a** and **7b** were identical with those reported in the literature.[6]

For the synthesis of *vibo*-quercitol **10,** one should introduce two hydroxyl group to the double bond in **5** in a trans fashion (Scheme 2). Therefore, we have submitted **5b** to epoxidation reaction[15] with *m*-chloroperbenzoic acid in an ultrasonic bath and obtained the epoxide in 94% yield as the sole product **8,** whose exact configuration was determined on the basis of NMR spectral data and NOE experiments. The directive effect of the hydroxyl group has been suggested to arise because of hydrogen bonding between the hydroxyl group and the attacking

Scheme 2



peracid.[16] The isolated epoxide **8** was submitted to acid-catalyzed ring-opening reaction in acetic anhydride and we have isolated a mixture consisting of *talo*-pentaacetates **7b** and *vibo*-pentaacetate **9**[15] in a ratio of 4:1. The resulting mixture has been separated on a silica gel column. Ammonolysis of **7b** and **9** furnished the corresponding quercitols.

Experimental Section

General Procedure. Melting points were determined on a melting apparatus. Infrared spectra were obtained from KBr pellets on an infrared spectrophotometer. ^{1}H NMR spectra were recorded on 200 MHz spectrometer and reported in δ units with $SiMe_4$ as internal standard. All column chromatography was performed on silica gel (60 mesh).

4-Cyclohexene-*cis*-1,2-diol (2). The reported procedure[12] was used for the synthesis of 4-cyclohexene-*cis*-1,2-diol **2** in 65% yield: mp 69−70 °C, colorless crystals from ethyl acetate:hexane (3:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.55 (m, 2H), 3.91 (m, 2H), 2.28 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 125.70, 70.90, 32.93.

(3a*R*,7a*S*)-2,2-Dimethyl-3a,4,7,7a-tetrahydrobenzo-1,3-dioxole (3). The described ketalization procedure in the literature[8a,17] was applied to the synthesis of **3** (colorless liquid, 96%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (m, 2H), 4.35 (m, 2H), 2.25 (m, 4H), 1.41 (s, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 126.00, 107.97, 73.56, 28.78, 27.49, 25.35.

(1a,4b,6a)-8,8-Dimethyl-7,9-dioxa-bicyclo[4.3.0^{1,6}]non-2-en-4-yl hydroperoxide 4. To a stirred solution of ketal **3** (1.0 g, 6.4 mmol) in 150 mL of CH_2Cl_2 was added 20 mg of tetraphenylporphyrin (TPP). The resulting mixture was irradiated with a tungsten halogen projection lamp (500 W) while oxygen was being passed through the solution and the mixture was stirred at room temperature for 12 h. Evaporation of the solvent (30 °C, 20 mmHg) and chromatography of the residue on a Florisil column (30 g) eluting with *n*-hexane/ CH_2Cl_2 (7:4) gave pure hydroperoxide **4** (1.15 g, 95%, colorless liquid): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.15 (s, 1H), 6.06 (dm, A part of AB system, J = 10.4 Hz, 1H), 5.95 (dm, B part of AB system, J = 10.4 Hz, 1H), 4.70 (m, 1H), 4.68 (m, 2H), 2.45 (dt, A part of AB system, J = 13.6, 3.9 Hz, 1H), 1.95 (ddd, B part of AB system, J = 13.6, 8.8, 2.8 Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 129.72, 129.46, 109.29, 77.21, 72.85, 71.85, 30.15, 28.24, 26.82; IR (KBr, cm^{-1}) 3462, 3387, 3004, 2953, 1651, 1472, 1395, 1242, 1165, 1063, 859.

(1a,4b,6a)-8,8-Dimethyl-4-hydroxy-7,9-dioxa-bicyclo-[4.3.0$^{1.6}$]non-2-ene 5a. To a magnetically stirred slurry of 0.82 g (10.7 mmol) of thiourea in 25 mL of methanol was added a solution of 1.00 g (5.37 mmol) of *anti*-hydroperoxide **4** in 50 mL of methanol at 25 °C. After complete of addition (ca. 10 min),

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the mixture was stirred for 1 h, the solid was removed by filtration, methanol was evaporated (35 °C, 20 mmHg), and the residue purified by column chromatography on silica gel (10 g) eluting with chloroform afforded pure **5a** (0.82 g, 90%, colorless liquid): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.86 (dm, A part of AB system, J = 11.4 Hz, 1H), 5.65 (ddd, B part of AB system, J = 11.4, 4.3, 2.4 Hz, 1H), 4.45 (m, 3H), 2.44 (ddm, A part of AB system, J = 13.8, 3.7 Hz, 1H), 1.95 (ddd, B part of AB system, J = 13.8, 9.5, 2.4 Hz, 1H), 1.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.34, 129.10, 109.30, 73.40, 71.91, 63.82, 35.83, 28.12, 26.35; IR (KBr, cm^{-1}) 3438, 3004, 2953, 2902, 1472, 1395, 1242, 1089, 1038, 885. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.30; H, 8.12.

(1a,4b,6a)-8,8-Dimethyl-4-acetoxy-7,9-dioxa-bicyclo[4.3.0$^{1.6}$]-non-2-ene 5b. To a magnetically stirred solution of alcohol **5a** (0.6 g, 3.50 mmol) in 3 mL of pyridine was added acetic anhydride (0.428 g, 4.2 mmol). The reaction mixture was stirred at room temperature for 8 h and cooled to 0 °C. After addition of 100 mL of water, the water phase was extracted with ether (3 × 50 mL). The combined organic extracts were washed with $NaHCO_3$ solution (10 mL) and water (5 mL) and then dried (Na_2SO_4). Removal of the solvent under reduced pressure gave acetate **5b** (0.59 g, 78%, colorless liquid): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.71 (dm, A part of AB system, J = 10.8 Hz, 1H), 5.65 (dm, B part of AB system, J = 10.8 Hz, 1H), 5.28 (m, 1H), 4.32 (m, 2H), 2.31 (ddt, A part of AB system, J = 13.8, 5.5, 1.1 Hz, 1H), 1.65 (ddd, B part of AB system, J = 13.8, 9.1, 2.8 Hz, 1H), 1.92 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.15, 130.05, 129.10, 109.12, 72.22, 71.83, 66.52, 31.80, 28.12, 27.82, 22.05; IR (KBr, cm^{-1}) 2990, 1740, 1370, 1240, 1040. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.93; H, 7.46.

(1a,2b,3b,4b,6a)-8,8-Dimethyl-2,3,4-triacetoxy-7,9-dioxa-bicyclo[4.3.0$^{1.6}$]nonane 6b. To a magnetically stirred ethanol solution (100 mL) of alkene **5b** (2.5 g, 11.79 mmol) was added a solution of $KMnO_4$ (1.86 g, 11.79 mmol) and $MgSO_4$ (1.41 g, 11.79 mmol) in water (40 mL) at −5 °C during 7 h. After the addition was completed, the reaction mixture was stirred for an 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 diol **6a** (1.630 g, 56%), which was submitted to acetylation as described above to give **6b** (1.92 g, 88%, colorless liquid): ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.41(m, 1H), 5.15 (ddd, J = 11.9, 5.5, 1.75 Hz, 1H), 4.95 (dd, J = 8.4, 2.5 Hz, 1H), 4.35 (m, 1H), 4.16 (dd, J = 11.9, 8.4 Hz, 1H), 2.30 (dd, A part of AB system, J = 14.2, 5.0 Hz, 1H), 2.13 (dd, B part of AB system, J = 14.2, 4.8 Hz,1H), 2.06 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H), 1.44 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.42, 170.37, 170.16, 109.92, 75.48, 73.09, 72.41, 70.92, 67.07, 28.47, 27.04, 26.54, 21.27; IR (KBr, cm^{-1}) 2993, 1740, 1435, 1360, 1250, 1060. Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.81; H, 6.54.

(1a,2a,3a,4b,5b)-Cyclohexanepentol [(±)-*talo*-Quercitol] 7a. Ketal triacetate **6b** (1.5 g, 4.5 mmol) was dissolved in 5 mL of 1 N H_2SO_4 and the resulting mixture was stirred at room temperature for 3 h. The acid was neutralized with $BaCO_3$. Filtration of the precipitate and evaporation of the solvent under reduced pressure gave *talo*-quercitol **7a** (0.7 g, 95%): mp 245−247 °C (lit.[6a] mp 246−248 °C) from EtOH; ^{1}H NMR (200 MHz, D_2O) δ 4.0 (m, 3H), 3.85 (m, 2H), 1.80 (dd, J = 9.7, 3.1, Hz, 2H); ^{13}C NMR (50 MHz, D_2O) δ 75.72, 73.38, 72.69, 70.82, 68.75, 35.17; IR (KBr, cm^{-1}) 3395, 2905, 2500, 1350, 1090, 1000, 845.

(1a,2a,3a,4b,5b)-Pentaacetoxycyclohexane [(±)-*talo*-Quercitol Pentaacetate] 7b. *talo*-Quercitol **7a** was submitted to acetylation as described above to give *talo*-quercitol pentaacetate **7b** (colorless solid, 85%): mp 169−171 °C (lit. mp 182−183 °C,[6] 169.5−171.5 °C[7]) from EtOH; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.61 (m, 1H), 5.51 (q, J = 3.2 Hz, 1H), 5.27 (dd, A part of AB system, J = 10.8, 2.72 Hz, 1H), 5.21 (dd, B part of AB system, J = 10.8, 3.2 Hz, 1H), 5.25 (m, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.04 (m, 2H), 2.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.72, 170.52, 170.45, 170.20, 70.07, 69.51, 68.20, 67.31, 66.56, 29.36, 21.45, 21.28, 21.19, 21.13; IR (KBr, cm^{-1}) 2995, 1745, 1370, 1230, 1045.

(1a,2b,4b,5b,7a)-9,9-Dimethyl-5-hydroxy-3,8,10-trioxa-tricyclo[5.3.0$^{2.4}$.0$^{1.7}$]decane 8. To a solution of alkene **5a** (1 g, 5.8 mmol) in 5 mL of CH_2Cl_2 were added 2 g of Na_2CO_3 and 1.7 g (6.96 mmol) of *m*-chloroperbenzoic acid (*m*-CPBA). The mixture was sonicated in an ultrasonic bath (50 kHz) for 3 h. The precipitate was filtered and washed with 50 mL of CH_2Cl_2. The combined CH_2Cl_2 solutions were filtered from a silica gel column (5 g) eluting with CH_2Cl_2. Evaporation of the solvent gave **8** (1.01 g, 94%): mp 60−61 °C, colorless solid from CH_2Cl_2; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.31 (m, 3H), 3.39 (br.d, A part of AB system, J = 4.00 Hz, 1H), 3.20 (dt, B part of AB system, J = 4.0, 1.1 Hz, 1H,), 2.15(ddd, J = 14.3, 5.6, 2.4 Hz, 1H), 1.61 (ddd, J = 14.3, 10,8, 1.4 Hz, 1H,), 1.40 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 109.66, 73.93, 70.35, 64.39, 56.38, 55.72, 27.98, 27.58, 25.72; IR (KBr, cm^{-1}) 3438, 3004, 2978, 1421, 1395, 1268, 1191. Anal. Calcd for $C_9H_{14}O_4$: C, 63.68; H, 8.25. Found: C,63.42; H, 8.11.

Acetolysis of Epoxy Ketal 8. Ketal **8** (500 mg, 2.68 mmol) was dissolved in 5 mL of acetic anhydride, to it was added 50 mg of concentrated H_2SO_4, and the resulting mixture was refluxed for 6 h. The mixture was added to 50 mL of water, extracted with ethyl acetate (3 × 50 mL), and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave a mixture consisting of *talo*-quercitol pentaacetate **7b** and *vibo*-quercitol pentaacetate **9** in a ratio of 80:20 determined by ^{1}H NMR (0.8 g, combined yield 80%). Pentaacetates **7b** and **9** were separated by column chromatography using silica gel and eluting with hexane:ethyl acetate (solvent composition was gradated from starting 85:15 to 75:25) to give *talo*-quercitol pentaacetate **7b** (0.508 g, 50%) and *vibo*-quercitol pentaacetate **9** (0.103 g, 10%): mp for **9**, 113−114 °C (lit. mp 126 °C,[19] 114 °C,[6a] 112−113 °C[18]) from ethanol; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.46 (dd, J = 3.4, 6.5 Hz, 1H,), 5.44 (t, J = 9.7 Hz, 1H), 5.28 (dd, J = 1.8, 4.3 Hz, 1H), 5.15 (q, J = 9.7 Hz, 1H), 4.94 (dd, J = 3.2, 10.3 Hz, 1H), 2.28 (dt, J = 4.3, 8.6 Hz, 1H), 2.14 (s, 3H), 2.01 (s, 6H), 2.00 (s, 3H), 1.98 (s, 3H), 1.75 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 171.79, 171.85, 171.72, 171.79, 171.66, 75.21, 73.43, 71.67, 70.37, 68.80, 32.74, 22.86, 22.76, 22.52; IR (KBr, cm^{-1}) 3489, 3029, 2953, 1753, 1446, 1395, 1242.

(1a,2a,3b,4b,5a)-Pentahydroxycyclohexane [(±)-*vibo*-Quercitol] 10. A 100 mg (0.26 mmol) portion of *vibo*-quercitol pentaacetate **9** was dissolved in 15 mL of methanol**.** While dry NH_3 was passed through the solution, the mixture was stirred for 2 h at room temperature. Evaporation of methanol and acetamide gave *vibo*-quercitol **10** (43 mg, quantitative): mp 161−162 °C (lit. mp 163 °C,[6a] 161−163 °C,[16] 159 °C[7]) from EtOH; ^{1}H NMR (200 MHz, D_2O) δ 4.07 (br q, J = 3.0 Hz, 1H), 3.77 (ddd, J = 12.0, 9.4, 4.8 Hz, 1H), 3.57 (t, J = 9.2 Hz, 1H), 3.50 (dd, J = 3.0, 9.2 Hz, 1H), 3.25 (t, J = 9.2 Hz, 1H), 2.10 (dt, J = 14.1, 3.9 Hz, 1H), 1.56 (ddd, J = 14.3, 12.1, 2.5 Hz, 1H); ^{13}C NMR (50 MHz, D_2O) δ 81.80, 78.12, 77.11, 72.77, 72.77, 39.44; IR (KBr, cm^{-1}) 3361, 2927, 1421, 1114, 1038, 987, 680.

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