Highly *Exo*-Selective Epoxidation and Hydroxylation of Triquinacene and Its Derivatives: *all-exo*-Hexahydroxytriquinane†

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Epoxidation of triquinacene **3** with dimethyldioxirane proceeded with a high degree of *exo*-face selectivity to give a quantitative yield of a 1:1.5 mixture of *all-exo*-**4a** and *endo,exo,exo*-triepoxytriquinane **4b**. Subsequent lithium aluminum hydride reduction of the *all-exo*-triepoxide **4a** gave *all-exo*-2,5,8-**5a** and *all-exo*-2,5,9-trihydroxytriquinane **5b**, respectively. The straightforward 3-fold dihydroxylation of triquinacene **3** led exclusively to the *all-exo*-hexahydroxytriquinane **8** in one step. X-ray crystal structure analyses confirmed the configuration of the triepoxide **4b** and the hexaacetate **9** of the hexol **8**.

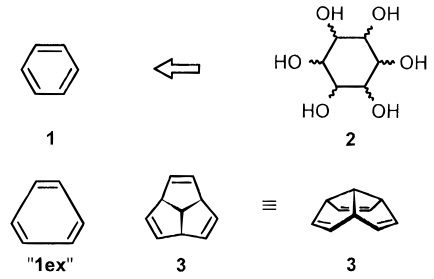
Introduction

Carbocyclic analogues of sugars, such as the hexahydroxycyclohexanes (inositols), can act as potent inhibitors of carbohydrate-metabolizing enzymes.[1] These molecules undoubtedly exert their biological activity by mimicking the corresponding sugar moiety. Owing to their carbocyclic ring their glycoside type derivatives are not subject to the action of hydrolase enzymes that cleave natural glycosidic bonds. Another biological importance of, for example, *myo*-inositol-1,4,5-triphosphate is its importance as a secondary messenger in living organisms.[2]

Stereoisomeric hexahydroxycyclohexanes **2** can be directly derived from benzene (**1**) (Scheme 1) in a one-pot synthesis. Unfortunately, this catalytic photoinduced charge-transfer osmylation forms a mixture of various isomers, with each isomer present in rather low yield, due to the planarity of the delocalized π-system in benzene.[3] Approaches toward other oligoepoxy- and oligohydroxycycloalkanes have been reported previously.[4] Similarly, no stereocontrol was observed, and mixtures of stereoisomers were obtained in all cases.

The C_{3v}-symmetric triquinacene (**3**), in which the three double bonds are being held apart by the carbine bridge,[5]

Scheme 1



can be viewed as an "expanded benzene" ("**1ex**"), but in contrast to benzene (**1**) its three localized double bonds have normal reactivity, and the molecule has a bowl shape. These are ideal prerequisites for *exo*-face selectivity in any electrophilic addition to its three double bonds. In this report we describe the highly selective synthesis of *all-exo*-triepoxy- and *all-exo*-oligohydroxytriquinane derivatives from readily accessible triquinacene **3**.[6]

Results and Discussion

Two different oxidants were utilized for the 3-fold epoxidation of triquinacene (**3**). While the common epoxidation with *m*-chloroperbenzoic acid[7] in the presence of $NaHCO_3$ as a buffer gave, after aqueous workup, a 1:1.3 mixture of diastereomers **4a,b** in 63% yield, the more recently developed milder method using a solution of dimethyldioxirane (DMDO) in acetone[8] afforded **4a** and **4b** in 85% yield. In both epoxidations, only two of four conceivable stereoisomers were produced. The absence of the bis-*endo*- and tris-*endo*-isomers clearly demonstrates the high *exo*-face selectivity in any addition to the bowl-shaped triquinacene molecule **3**. It appears that

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§ On leave from the Université de Paris VI, Jussien.

|| Institut für Anorganische Chemie der Universität Göttingen, X-ray structure analyses.

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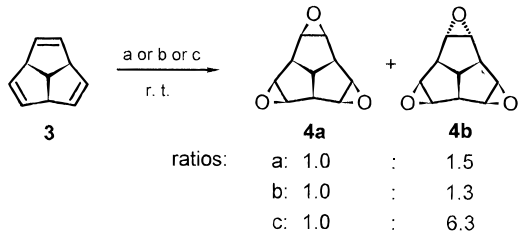
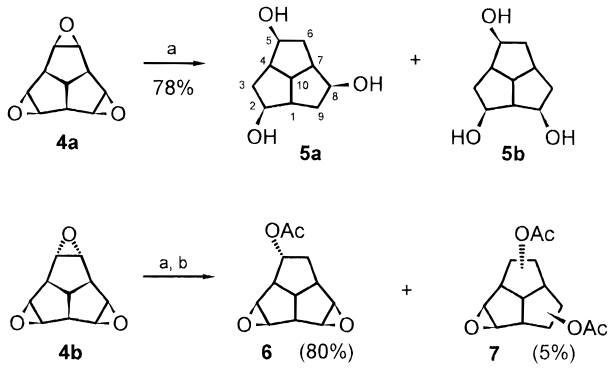
Scheme 2[a]



[a] (a) DMDO, acetone, quant; (b) MCPBA, $NaHCO_3$, CH_2Cl_2, 63%; (c) oxone, $NaHCO_3$, acetone, H_2O, 58%.

Scheme 3[a]



[a] (a) LAH, THF, reflux; (b) Ac_2O, NEt_3, DMAP (cat.), 70 °C.

only the third epoxidation step can go with *exo*- or *endo*-attack, as only one GC peak each for the mono- and diepoxide of **3** could be observed while the reaction was in progress. The ratios of the triepoxides **4a** and **4b** could easily be determined both from the gas chromatogram (GC) and the ^{1}H NMR spectrum of the crude reaction mixture (see Scheme 2). The two triepoxides **4a** and **4b** were separated by column chromatography, eluting with a 1:1 mixture of diethyl ether and *tert*-butyl methyl ether. Epoxidation of **3** with in situ generated dimethyldioxirane using Caroat ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) and $NaHCO_3$ in acetone/dichloromethane/water (two-phase system) yielded, after flash chromatographic separation, 50% of **4b** and 8% of **4a**.[9]

To confirm the configurational assignments for the two stereoisomers **4a,b**, an X-ray crystal structure analysis of the major triepoxide **4b** was performed.[10] This clearly proves the *endo,exo,exo*-configuration for **4b**. It is beyond reasonable doubt that the other isomer, which must be C_3-symmetric according to its ^{1}H and ^{13}C NMR spectra, can only be the *all-exo*-stereoisomer **4a** (see Scheme 2).

The epoxidations of cyclohexane-annelated triquinacene derivatives have recently been reported and showed different selectivities.[11]

Reductive ring opening of epoxides with lithium aluminum hydride (LAH) leads to alcohols. On treatment of the *all-exo*-triepoxytriquinane **4a** with an excess of

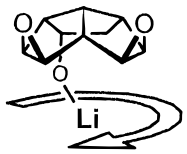
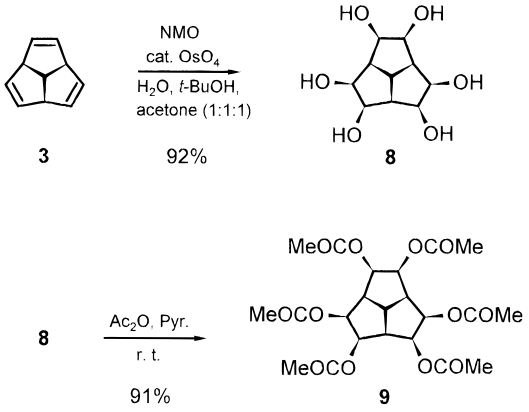


Figure 1. Solvated lithium ion as a potential blocker for further reduction.

Scheme 4



LAH, the two isomeric triols **5a** and **5b** were obtained in 78% yield (Scheme 3). The preparation of these triols has previously been achieved via hydroboration of triquinacene **3** by Paquette et al.[12] As reported, the separation of **5a** and **5b** is difficult and requires a 2 m long HPLC column,[12] and derivatives of **5a,b** are difficult to be separated as well.[13]

Surprisingly, the reduction of the *endo,exo,exo*-triepoxide **4b** can be interrupted at an early stage. The major product isolated after treatment of the crude product with acetic anhydride in the presence of triethylamine was the monoacetoxy-*exo,exo*-diepoxide **6** (80%). Only a trace (5%) of a diacetoxy compound **7** was observed (Scheme 3). It may be speculated that the first attack of LAH occurs from the *exo*-side of the molecule opening selectively the *endo*-epoxy ring to give an intermediate lithium alkoxide (see Figure 1). The lithium cation, which probably is solvated by THF molecules and placed on the *endo*-oxyanion group, might efficiently block the *endo*-face of the molecule, from where further hydride transfer from LAH would have to occur.

Quite generally alkenes can be vicinally dihydroxylated with osmium tetraoxide (catalytic) and *N*-methylmorpholine *N*-oxide in an acetone/*tert*-butyl alcohol/water (1:1:1) mixture.[14] The application of this protocol to triquinacene (**3**) gave an excellent yield (92%) of the *all-exo*-hexahydroxytriquinane **8** (Scheme 4). Although the hexol **8** is readily water-soluble, it partially precipitated from the reaction mixture due to its poor solubility in the composite solvent mixture. Compound **8** was further purified by recrystallization from ethanol/water. Unfortunately the crystals obtained were not suitable for an X-ray structure analysis. However, the very simple ^{1}H and ^{13}C NMR spectra of the product strongly corroborate its unique structure as that of the C_3-symmetric hexol **8**.

(9) In this epoxidation the conversion was not complete and 16% of the *exo,exo*-triquinacene diepoxide (R_f = 0.45) were isolated.

(10) The authors have deposited atomic coordinates for **4b** and **9a** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Centre, 12 Union Road, CB2 1EZ, UK. (a) Sheldrick, G. M. *Acta Crytallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M, SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.

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With the aim to eventually obtain a X-ray structural analysis of a suitable derivative, the hexol **8** was acetylated with acetic anhydride in the presence of pyridine (Scheme 4). Recrystallization of the *all-exo*-hexaacetoxytriquinane **9** from tetrahydrofuran gave X-ray suitable crystals. The crystal structure analysis did not only decisively prove the *all-exo* configuration of the hexol **8**, but also disclosed a remarkable distortion of the tricyclo-[5.2.1.$0^{4,10}$]decane skeleton. To avoid prohibitively short nonbonded contacts in a fully eclipsed orientation, all three C_2 bridges are twisted by 41° leaving the molecule with overall C_3 rather than C_{3v} symmetry. A slight disorder problem was observed, even when new crystals grown from a pentane solution were investigated. However, this disorder only affected one of the six acetoxy groups, with 65% of the molecules having one and 35% a slightly different orientation of this group.

Experimental Section

General Remarks. ^{1}H and ^{13}C NMR were measured at 250, 300, or 500 MHz and 62.9, 67.9, 75.5, 100.6, or 125.7 MHz, respectively, in D_2O or $CDCl_3$ with Me_4Si as the internal standard. For DEPT spectra primary and tertiary carbons are designated as + and secondary carbons as −; missing DEPT signals are designated C_{quat}. Infrared (FT-IR) spectra were measured using KBr plate. HRMS were determined using preselected ion peak matching at $R \sim 10000$ to be within ±2 ppm of the exact mass. Column chromatography: Silica gel 60 (70−230 mesh, E. Merck, Darmstadt). Flash chromatography: Silica gel, chromatography medium 60 (20−45 μm, Amicon). Thin-layer chromatography (TLC): Alugram Sil G/UV_{254} (Macherey-Nagel, Düren). Elemental analyses: Mikroanalytisches Laboratorium, Institut für Organische Chemie der Georg-August-Universität Göttingen. Solvents used were dried by refluxing over sodium and distilled immediately before use. All reactions were carried out under an inert atmosphere in oven-dried glassware. Triquinacene (**3**) was prepared according to the published procedure.[6b] Dimethyldioxirane was freshly prepared from Caroat ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) and $NaHCO_3$ in acetone/water following the published procedure.[8]

***all-exo*-2,3:5,6:8,9-Triepoxytricyclo[5.2.1.$0^{4,10}$]decane (4a) and *endo,exo,exo*-2,3:5,6:8,9-Triepoxytricyclo[5.2.1.$0^{4,10}$]-decane (4b) (Triquinacene Triepoxides)**: Epoxidation of triquinacene (**3**) with a dimethyldioxirane (DMDO) solution in acetone.

Triquinacene (**3**; 475 mg, 3.65 mmol) was added with stirring to a solution of dimethyldioxirane in acetone (300 mL, 0.09 M, 27 mmol) for 3 h at 25 °C. The mixture was concentrated in vacuo to yield 648 mg of crude triepoxides **4a**,**b** which were separated by flash column chromatography (*t*-BuOMe/PE 1:1, column 40 × 2 cm). **4b** (R_f = 0.18) 321 mg (49%) colorless crystals, mp 133 °C: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.67 [d, ^3J = 2.3 Hz, 2 H, 6(8)-H], 3.60 [d, ^3J = 2.3 Hz, 2 H, 5(9)-H], 3.52 [d, ^3J = 2.0 Hz, 2 H, 2(3)-H], 3.02 (dt, ^3J = 9.2, 8.1 Hz, 1 H, 10-H), 2.86 [m_c, 3 H, 1(4,7)-H]. ^{13}C NMR (127.5 MHz, $CDCl_3$, DEPT): δ = 61.3 [+, C-2(3)], 60.8 [+, C-5(9)], 59.0 [+, C-6(8)], 56.0 (+, C-10), 48.1 (+, C-7), 47.4 [+, C-1(4)]. IR (KBr): ν = 3051 cm^{-1}, 3024, 3002, 2945, 2923, 1387, 1272, 1263, 1224, 1072. MS (70 eV, EI): *m*/*z* (%) = 178 [M^+] (6), 162 (3), 149 (7), 133 (8), 131 (9), 121 (13), 103 (27), 91 (36), 81 (68), 78 (100), 77 (52). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.54; H, 5.64. Single crystals were obtained by recrystallization from ethyl acetate. **4a** (R_f = 0.13) 232 mg (36%) colorless crystals, mp >250 °C: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.51 [s, 6 H, 2(3,5,6,8,9)-H], 2.98 [d, ^3J = 7.7 Hz, 3 H, 1(4,7)-H], 2.73 (q, ^3J = 7.7 Hz, 1 H, 10-H). ^{13}C NMR (125.7 MHz, $CDCl_3$, DEPT): δ = 59.9 [+, C-2(3,5,6,8,9)], 54.6 (+, C-10), 48.5 [+, C-1(4,7)]. IR (KBr): ν = 3038 cm^{-1}, 3006, 2934, 1396, 1238, 1079. MS (70 eV, EI): *m*/*z* (%) = 179 (4), 178 [M^+] (23), 149 (9), 135 (6), 131 (10), 121 (28), 107 (13), 105 (24), 104 (12), 94 (21), 91 (29), 81 (100), 78 (52). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.37; H, 5.56.

Epoxidation of Triquinacene (3) with In Situ Generated DMDO Using Caroat under Buffered Conditions. A 50 mL buffered Caroat solution was prepared by neutralizing a solution of 9.43 g (15.4 mmol) of Caroat in 45 mL of water with 4.0 g (48 mmol) of $NaHCO_3$ (pH-control).

To a solution of 263 mg (2.02 mmol) of triquinacene (**3**) in 5 mL of CH_2Cl_2 and 10 mL of acetone was added over 3 h 50 mL of a buffered cold (0 °C) Caroat solution in five portions at 0 °C. The reaction was monitored by GLC. After diluting the reaction mixture with 40 mL of H_2O it was extracted with two portions (20 mL) of CH_2Cl_2, and after saturating the inorganic phase with NaCl the solution was extracted with three portions (20 mL) of diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give 479 mg of crude products, which were separated by flash chromatography (*t*-BuOMe/PE 1:1, column 16 × 2 cm, 26 g of silica gel):[9] *exo,exo*-triquinacene diepoxide (R_f = 0.45), 50 mg (16%) colorless crystals: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.67 [s, 2 H, 8(9)-H], 3.41 [m_c, 4 H, 2(3,5,6)-H], 3.37 [d, ^3J = 8.0 Hz, 2 H, 1(7)-H], 3.01 (d, ^3J = 8.0 Hz, 1 H, 4-H), 2.88 (q, ^3J = 8.0 Hz, 1 H, 10-H). **4b** (R_f = 0.18) 180 mg (50%). **4a** (R_f = 0.13) 29 mg (8%).

***all-exo*-2,5,8-Trihydroxytricyclo[5.2.1.$0^{4,10}$]decane (5a) and *all-exo*-2,5,9-Trihydroxy-tricyclo[5.2.1.$0^{4,10}$]decane (5b) (Triquinanetriols)**:[12,13] A solution of the triepoxide **4a** (215 mg, 1.21 mmol) in 10 mL of anhydrous THF was added dropwise to a stirred suspension of $LiAlH_4$ (400 mg, 10.5 mmol) in 10 mL of anhydrous THF under an argon atmosphere. The mixture was heated under reflux for 24 h and then cooled to 0 °C. The excess hydride was destroyed with 1 mL of 1 N NaOH. The colorless precipitate was removed by filtration, and the filtrate was concentrated. The crude yellow oil was purified by column chromatography (CH_2Cl_2/MeOH 0:1 to 1:1, column 40 × 2 cm) to yield 173 mg (78%) of a mixture of the triols **5a** and **5b** (1:2). As reported by Paquette et al.[12] these triols can only be separated with great efforts (2 m HPLC column). For spectroscopic data see ref 11.

8-*endo*-Acetoxy-*exo,exo*-2:3,5:6-diepoxytricyclo[5.2.1.$0^{4,10}$]-decane (6) and 5,8-Diacetoxy-*exo*-2:3-epoxytricyclo-[5.2.1.$0^{4,10}$]decane (7): A solution of triepoxide **4b** (312 mg, 1.75 mmol) in 10 mL of anhydrous THF was added dropwise to a stirred suspension of $LiAlH_4$ (400 mg, 10.5 mmol) in 10 mL of anhydrous THF under an argon atmosphere. The reaction mixture was heated under reflux for 3 h and then cooled to 0 °C. The excess hydride was destroyed with 1 mL of 1 N NaOH. The colorless precipitate was removed by filtration, and the filtrate was concentrated. The crude yellow oil (320 mg) was directly converted into its acetate by refluxing it for 3 h in a mixture of triethylamine (10 mL), acetic anhydride (3 mL), and 50 mg of *N*,*N*-dimethyl-4-aminopyridine. Then the mixture was cooled to 0 °C and after addition of 15 mL of water was extracted with ether (5 × 20 mL). The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (ethyl acetate/light petroleum 1:1, columm 40 × 2 cm) to yield 311 mg (80%) of **6** as colorless crystals, mp 63 °C (R_f = 0.32). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.90 (s, 1 H), 4.35 (s, 1 H), 4.05 (s, 1 H), 3.70 (s, 1 H), 3.45 (s, 1 H), 3.00 (s, 1 H), 2.80−2.40 (m, 3 H), 2.10 (s, 3 H, CH_3), 1.80 (d, ^3J = 10.3 Hz, 1 H), 1.75 (d, ^3J = 10.3 Hz, 1 H). ^{13}C NMR (127.5 MHz, $CDCl_3$, DEPT): δ = 169.7 (C_{quat}, C=O), 84.8 (+), 77.6 (+), 76.9 (+), 59.4 (+), 56.8 (+), 53.4 (+), 51.4 (+), 46.1 (+), 44.1 (+), 38.3 (+), 20.8 (−). IR (KBr): ν = 3460 cm^{-1}, 3020, 2850, 1733, 1183. MS (70 eV, EI): *m*/*z* (%) = 222 [M^+] (9), 162 (81), 133 (92), 94 (96), 81 (94), 43 (100). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4. Found: C, 64.9; H, 6.5. In addition 23 mg (5%) of the diacetate **7** was isolated (R_f = 0.45). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.40 (d, ^3J = 5.5 Hz, 1 H), 4.82 (s, 1 H), 3.95 (bs, 2 H), 2.92 (s, 2 H), 2.66−2.55 (m, 1 H), 2.37 (d, ^3J = 6.5 Hz, 1 H), 2.20−2.05 (m, 1 H), 2.00 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 1.90−1.60 (m, 2 H), 1.38 (d, ^3J = 5.8 Hz, 1 H). ^{13}C NMR (127.5 MHz, $CDCl_3$, DEPT): δ = 170.1 (C_{quat}, C=O), 169.7 (C_{quat},

C=O), 84.4 (+), 84.2 (+), 81.0 (+), 78.4 (+), 56.5 (+), 49.9 (+), 49.2 (+), 47.4 (+), 40.1 (−), 30.9 (−), 21.2 (+), 20.9 (+). MS (70 eV, EI): *m/z* (%) = 266 [M^+] (0.5), 206 [M − HOAc]$^+$ (22), 164 (100), 146 (28). HRMS for $C_{14}H_{18}O_5$: 266.1154 (correct molecular mass).

***all-exo*-2,3,5,6,8,9-Hexahydroxytricyclo[5.2.1.0^{4,10}]-decane (8) (Hexahydroxytriquinane)**: To a mixture of *tert*-butyl alcohol (3 mL), water (3 mL), *N*-methylmorpholine *N*-oxide (2.10 g, 18.0 mmol), and $K_2OsO_4{\cdot}2H_2O$ (30 mg), was added triquinacene (**3**) (360 mg, 2.76 mmol) in 3 mL of acetone slowly at 10 °C. The mixture was stirred overnight, and a white solid precipitated. The solid was filtered off and washed with acetone. The filtrate was diluted with acetone to give two phases, the lower of which still contained a considerable amount of the hexaalcohol. After evaporation of the solvent from this lower phase and recrystallization of the residue from ethanol/water, 589 mg (92%) of **8** was obtained as yellow crystals, mp >250 °C. ^{1}H NMR (250 MHz, D_2O): δ = 4.60 (s, 6 H, HDO from exchange), 3.68 [d, ^3J = 3.8 Hz, 6 H, 2(3,5,6,8,9)-H], 3.12 (q, ^3J = 10.0 Hz, 1 H, 10-H), 2.15−2.05 [m, 3 H, 1(4,7)-H]. ^{13}C NMR (125.7 MHz, D_2O, DEPT): δ = 75.4 [+, C-2(3,5,6,8,9)], 51.4 [+, C-1(4,7)], 43.2 (+, C-10). IR (KBr): ν = 3649 cm^{-1}, 3368, 3087, 2957, 2777, 1232, 1021. MS (DCI, NH_3): *m/z* (%) = 251/250 [M + NH_4^+] (11/100), 232 [M^+] (22), 214 (24), 196 (16).

***all-exo*-2,3,5,6,8,9-Hexacetoxytricyclo[5.2.1.0^{4,10}]-decane (9) (Hexacetoxytriquinane)**: To a stirred mixture of acetic anhydride (733 μL, 792 mg, 7.76 mmol) and anhydrous pyridine (626 μL, 614 mg, 7.76 mmol) in a 50 mL beaker was added 90 mg (0.39 mmol) of hexahydroxytriquinane **8**. The flask with the reaction mixture was placed in a desiccator containing two 25 mL beakers, one filled with KOH pellets and the other one with concentrated H_2SO_4. The reaction mixture was stirred for 48 h at room temperature and 200 Torr and then 24 h at 0.01 Torr. The residue was obtained as a brown solid (190 mg). Recrystallization from EtOH yielded 173 mg (91%) of **9a** as colorless needles, mp 225 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.17 [d, ^3J = 4.0 Hz, 6 H, 2(3,5,6,8,9)-H], 3.55 (q, ^3J = 10.3 Hz, 1 H, 10-H), 2.69 [dt, ^3J = 10.3, ^3J = 4.0 Hz, 3 H, 1(4,7)-H], 2.03 (s, 18 H, −OCH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$, DEPT): δ = 169.7 (C_{quat}, C=O), 75.2 [+, C-2(3,5,6,8,9)], 48.6 [+, C-1(4,7)], 43.2 (+, C-10), 20.7 (+, OCH_3). IR (KBr): ν = 3472 cm^{-1}, 2940, 1747, 1437, 1372, 1199, 1078, 1027. MS (70 eV, EI): *m/z* (%) = 485 [M^+ + 1] (<1), 425 [M^+ − OAc] (2), 365 (11), 322 (56), 262 (68), 220 (44), 160 (48), 132 (26), 43 [OAc^+] (100). Anal. Calcd for $C_{22}H_{28}O_{12}$: C, 54.54; H, 5.83. Found: C, 54.64, H, 5.86.

X-ray Crystal Structure Analyses of Compounds 4b and 9.[10] The X-ray data at 150 K were collected on a Stoe-AED2 four circle diffractometer, Mo K_α radiation. The calculations were done using the SHELXTL program. The X-ray data at 133 K were collected on a Stoe-Siemens-Huber four circle diffractometer, Mo K_α radiation. The calculations were done using the SHELXTL program.

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Supporting Information Available: ORTEP drawings for **4b** and **9** and details of the data acquisition (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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