was dissolved in 5% potassium acetate in methanol (25 ml) and heated (reflux) with stirring for 11 hr. The solution was poured into saturated aqueous sodium chloride (100 ml) and extracted with chloroform. The combined extract was dried and solvent was removed *in vacuo* to yield 161 mg of yellow solid. Purification by plc (4:1 benzene–acetone mobile phase) provided 100 mg of pale yellow oil which solidified on standing. A second plc purification (2:1 benzene–acetone mobile phase) afforded 51 mg of β epoxide **8**: pmr δ 1.00 (s, 19 methyl), 1.10 (s, 18 methyl), 3.37 (d, $J < 0.5$ Hz, 1 H, H-15), 2.95–3.97 (complex, $-CH_2OCH_2-$), 4.08 (br, 1 H, H-3).

To a stirred suspension of lithium aluminum hydride (400 mg) in refluxing tetrahydrofuran (40 ml) was added (dropwise) a solution of the β epoxide **8** in tetrahydrofuran (10 ml, under nitrogen). After 3 hr the solution was cooled (ice bath), a few drops of water were added, and then the solution was filtered at room temperature. Solvent was removed and the residue was dissolved in chloroform. The solid products were extracted with chloroform and the extract was washed with water, dried, and evaporated to yield 44 mg of crude product. The solid was combined with 20 mg of crude product from a previous experiment and purified by plc (2:1 benzene–acetone mobile phase) to give 44 mg of clear oil. A second plc purification (3:2 benzene–acetone mobile phase) gave 25 mg of **3β,14-dihydroxy-23-deoxo-5β,14β,20ξ-cardanolide** (**10a**) as a colorless solid. Several recrystallizations from ethanol–water afforded an analytical specimen as needles: mp 163–173°; ir 3420 (–OH), 1040 cm^{-1} (COC); pmr δ 0.95 (s, 19 methyl), 1.02 (s, 18 methyl), 3.10–3.95 (complex, $-CH_2OCH_2-$), 4.08 (br, 1 H, H-3); mass spectrum *m/e* (rel intensity) 362 (M^+, 9), 344 (65), 329 (34), 326 (24), 311 (23), 275 (26), 274 (100), 273 (34), 272 (61), 259 (17), 258 (18), 257 (31), 256 (23), 255 (35), 250 (11), 241 (16).

Anal. Calcd for $C_{23}H_{38}O_3$ (362.5): C, 76.20; H, 10.56. Found: C, 76.41; H, 11.22.

Registry No.—**3a**, 32970-98-2; **4**, 32970-99-3; **5**, 32971-00-9; **6**, 32971-01-0; **8**, 33020-99-4; **9**, 32971-02-1; **10a**, 32971-04-3; **10b**, 32971-04-3.

Photochemical Addition of Acetone to D-Glucal Triacetate and Subsequent Oxetane Ring Cleavage[1]

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3,7-Anhydro-1-deoxy-2-*C*-methyl-2-*O*-methyl-D-*glycero*-D-*ido*-octitol (**3**) and 3,7-anhydro-1,2-dideoxy-2-methylene-D-*glycero*-D-*ido*-octitol (**4**) are obtained from acid-catalyzed methanolysis of 5,6,8-tri-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**1**), obtained from ultraviolet irradiation of 3,4,6-tri-*O*-acetyl-D-glucal in acetone. Oxetane ring opening in benzene affords **4**. Ethanolysis of **1** yields the 2-*O*-ethyl derivative **5** in addition to **4**. Saturation of the methylene group in **4** followed by acetylation yields crystalline 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**10**). Benzylidenation of deacetylated **1** gives the 2,4:6,8-di-*O*-benzylidene derivative **6**.

Cycloaddition of carbonyl compounds to olefins leading to oxetane ring formation in the presence of ultraviolet irradiation has been extensively examined in aliphatic and aromatic compounds.[2-4] We have examined the photoaddition of acetone to 3,4,6-tri-*O*-acetyl-D-glucal and also have characterized the products obtained from opening of the produced oxetane ring.

Ultraviolet irradiation of 3,4,6-tri-*O*-acetyl-D-glucal in acetone at 10–15° for 5 hr gives 5,6,8-tri-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**1**) as the major product in 33% yield. The oxetane ring is thought to be formed through a stable biradical intermediate.[2] It is expected that carbon–oxygen bond formation at C-2 of the glucal predominates over its formation at C-1, because a carbon radical at C-1 has higher stability than a radical at C-2 of the sugar. Attachment at C-2 would be expected to position the oxygen trans to the acetoxy group at C-3. The dimethyl radical group presumably joins with the radical at C-1 to develop a ring of minimum strain resulting in the formation of the D-*glycero*-D-*ido*-octitol derivative. The gross structure of **1** may be assigned with the aid of nmr spectroscopy.[4] The signal of H-4 in the oxetane ring gives a quartet at τ 5.42 with $J_{4,5} = 3.5$ Hz and $J_{3,4} = 5.5$ Hz. Irradiation of the H-4 proton signal collapses the quartet ($J_{4,5} = 3.5$; $J_{5,6} = 9$ Hz) at τ 4.87 into a doublet with 9-Hz coupling constant. A triplet at τ 5.22 is due to H-6 and the signal of H-3 is superimposed in the τ 5.60–6.15 region which integrates for four protons.

Acid-catalyzed ring opening of oxetane rings has been reported.[2] However, deacetylation of **1** with 0.1 *N* sodium methoxide followed by deionization with excess Amberlite IR-120H at 25° for 16 hr affords a mixture of **3** and **4**, separated by column chromatography, in 45 and 10% yield, respectively. The oxetane ring of **2** is acid labile and is opened on a silica gel column eluted with chloroform–methanol, giving a mixture containing **3** and **4** in 10% yield. Compounds **3** and **4** can also be obtained by refluxing **1** in methanol in the presence of IR-120H; the yields of **3** and **4** are 41 and 14%, respectively. Treatment of **1** with IR-120H resin in benzene gives a 33% yield of the methylene derivative **4**. Ethanolysis of **2** at 25° in the presence of IR-120H resin for 16 hr provides a 34% yield of the methylene derivative **4** and a 21% yield of **5**. When direct ethanolysis is performed on **1** under reflux, the main product is the unsaturated octitol **4** (40%), while the *O*-ethyl derivative **5** is isolated in only 9% yield. Reaction of **2** with benzaldehyde and zinc chloride gives the 2,4:6,8-di-*O*-benzylidene compound **6** which is further characterized as its acetate **7**.

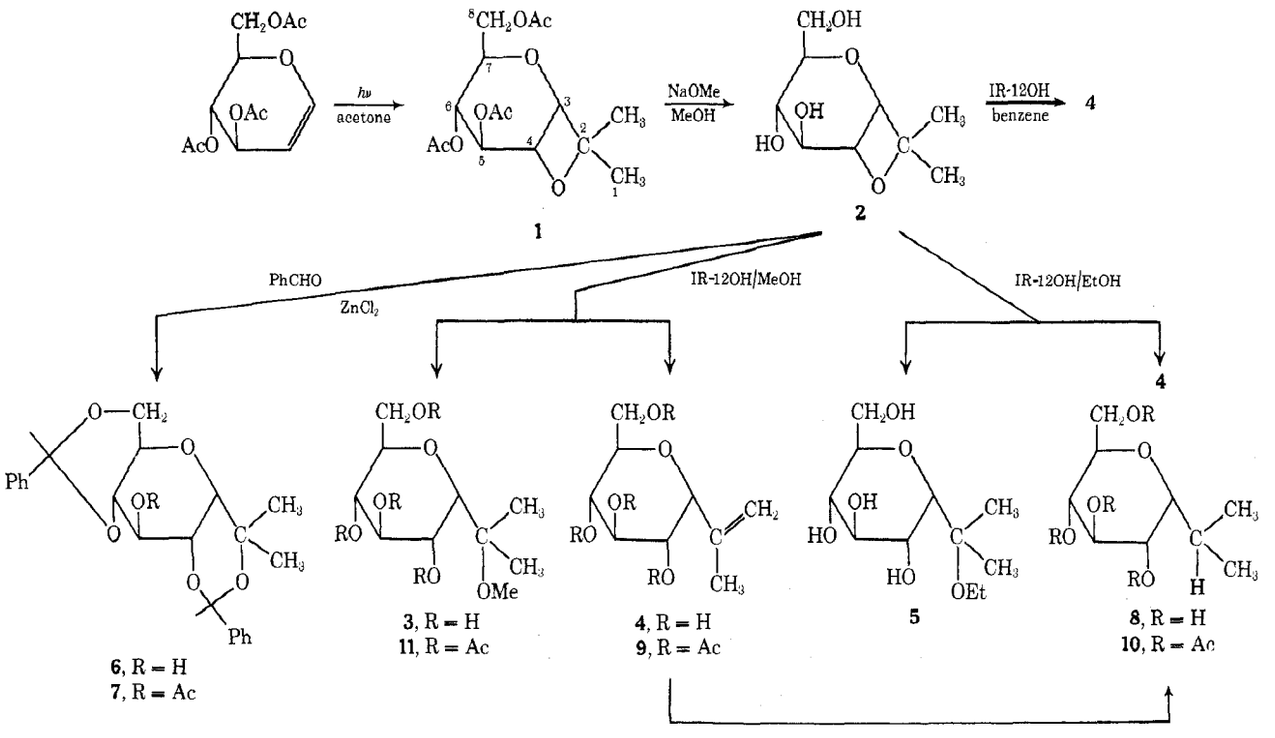
The nmr spectra of **4** and **8** permit assignment of structures. The methylene signals of **4** appear at τ 4.75, while these signals disappear in the reduction product **8**. In the nmr spectrum of **8**, resonance for the methine proton (H-2) appears as a multiplet around τ 8.20. The nmr spectrum of **3** demonstrates

(1) Journal Paper No. 4458 of the Purdue Agricultural Experiment Station.

(2) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954).

(3) D. R. Arnold, *Advan. Photochem.*, **6**, 31 (1968).

(4) N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, **93**, 1277 (1971).



signals with seven-proton intensity in the τ 5.95–6.60 region and a methoxy peak at τ 6.78. Because of overlapping of the signals in these spectra, they cannot be used to deduce the configuration at C-4 or at C-3. Evidence indicating that the substituent at C-4 is trans to that of C-5 may be deduced from the nmr spectrum of 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-2-methylene-D-*glycero*-D-*ido*-octitol (**9**). Here the proton at C-3 appears as a multiplet at τ 6.20, and the methylene protons give signals at τ 4.75. There is a quartet at τ 4.95, with spin–spin couplings of 9 and 5 Hz. Irradiation of the multiplet at τ 6.20 results in collapse of the quartet at τ 4.95 to a doublet ($J_{4,5}$ = 9 Hz) and irradiation of the quartet at τ 4.95 decreases the multiplicity at τ 6.20. Thus, the quartet at τ 4.95 is attributable to H-4. Since H-4 is trans diaxial to either H-3 or H-5 and is axial–equatorial to the other and since H-5 is axial, H-3 must be equatorial. Additional evidence for the axial orientations of these two protons is provided by nmr analysis of **11**. Signals for H-3, H-6, and H-5 appear respectively at τ 6.18 (doublet), 5.10 (triplet), and 4.40 (triplet). A quartet at τ 4.82 has the coupling constants 4.5 and 8 Hz. Irradiation of the doublet at τ 6.18 (H-3, $J_{3,4}$ = 4.5 Hz) collapses the quartet at τ 4.82 into a doublet with an 8-Hz splitting. Therefore, the quartet at τ 4.82 is assigned to H-4 and the larger J value must arise from the coupling of H-4 and H-5, configurational findings in **9**, and the configuration of **1** is hence D-glycero-D-ido.

Hydrogenation of the unsaturated acetate **9** using palladium on charcoal gives crystalline 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**10**), identical with the product obtained from the acetylation of **8** in pyridine with acetic anhydride. It is interesting to note that this is the first time a crystalline product has been obtained by C-alkylation of carbon C-1 of a sugar. C-1 alkylation of acetohalo sugars employing Grignard reagents, such as butyl and isopropyl,[5] fails to give crystalline products possible because a mixture of isomers is produced in each instance.

Experimental Section

Irradiations were made with a 450-W Hanovia 679A-36 mercury lamp in a quartz immersion well without filter under oxygen-free nitrogen. The progress of reactions and purity of products were checked by thin layer chromatography (tlc) on silica gel G[6] coated glass plates (5 × 13 cm) irrigated with (A) benzene–ethyl acetate (4:1 v/v) or (B) chloroform–methanol (9:1 v/v). Melting points were determined on a Fisher-Johns apparatus and were corrected. Infrared spectra were recorded in Nujol with a Perkin-Elmer Model 337 spectrometer, and nmr spectra were determined in deuteriochloroform (TMS as internal standard) and deuterium oxide (DSS as internal standard), unless otherwise mentioned, using Varian Associates A-60 or A-60A spectrometers. Optical rotations were measured at 25° in a Perkin-Elmer automatic polarimeter Model 141

5,6,8-Tri-*O*-acetyl-2,4:3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (1).—A solution of 3,4,6-tri-*o*-acetyl-D-glucal[7] (10 g) in 180 ml of acetone was irradiated for 5 hr at 10–15°, after which the solution was concentrated to a syrup. The syrup was applied to a silica gel[8] column (450 g) and eluted with benzene–ethyl acetate (95:5 v/v). Progress was checked by tlc using solvent A and the fractions containing the starting material, D-glucal triacetate (4.65 g), and **1** (2.05 g), were separately collected. The yield of **1**, based on the amount of starting material consumed, was 33%: $[\alpha]^{26}D$ + 54.1° (*c* 1.0, $CHCl_3$); nmr (CCl_4) τ 4.87 (q, 1, $J_{4,5}$ = 3.5, $J_{5,6}$ = 9 Hz, H-5), 5.22 (t, 1, $J_{5,6} = J_{6,7}$ = 9 Hz, H-6), 5.42 (q, 1, $J_{4,5}$ = 3.5, $J_{3,4}$ = 5.5 Hz, H-4), 7.98–8.02 (three s, OAc), 8.60 and 8.64 (two s, CCH_3).

Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.55; H, 6.71. Found: C, 54.30; H, 7.00.

3,7-Anhydro-1-deoxy-2-*C*-methyl-2-*O*-methyl-D-*glycero*-D-*ido*-octitol (3) and 3,7-Anhydro-1,2-dideoxy-2-methylene-D-*glycero*-D-*ido*-octitol (4). A. From Methanolysis of Deacetylated 1.—Compound **1** (1.62 g) was deacetylated in absolute methanol (50 ml) with 0.1 *N* sodium methoxide (10 ml) at 0°. Deacetylation was completed overnight at 25°. The reaction mix-

(5) C. D. Hurd and W. A. Bonner, *J. Amer. Chem. Soc.*, **67**, 1972 (1945).
(6) E. Merck, Darmstadt, Germany. Distributors: Brinkmann Instruments Inc., Westbury, N. Y. 11590.
(7) Pfanstiehl Laboratories, Inc., Waukegan, Ill.
(8) J. T. Baker Chemical Co., Phillipsburg, N. J.

ture was then deionized with Amberlite IR-120H (methanol-washed and air-dried) until neutral and then an additional 6 ml of the resin was added and stirred at 25° for 16 hr. After filtration, the resin was washed thoroughly with methanol and the combined filtrate was evaporated to a syrup which was applied to a silical gel column (30 g) and eluted with chloroform–methanol (95:5 v/v) to give 0.52 g of **3**, crystallized from ethyl acetate–hexane: mp 141–142°; $[\alpha]^{25}D$ +39.9° (*c* 1.0, CH_3OH); yield 45%; nmr (D_2O) τ 5.95–6.60 (m, 7, H-3, H-4, H-5, H-6, H-7, and H-8,) 6.78 (s, 3, OMe), 8.70 (s, 6, CCH_3).

Anal. Calcd for $C_{10}H_{20}O_6$: C, 50.83; H, 8.53. Found: C, 50.67; H, 8.55.

Further elution of the column gave 0.101 g of **4**, crystallized from ethyl acetate: mp 150–152°; $[\alpha]^{25}D$ +35.9° (*c* 1.0, CH_3OH); yield 10%; ν_{max} 1640 cm^{-1} (methylene); nmr (D_2O) τ 4.75 (m, 2, methylene), 5.60 (m, 1, H-3), 6.0–7.80 (m, 6, H-5, H-6, H-7, and H-8), 8.25 (s, 3, CCH_3).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.89. Found: C, 52.76; H, 7.84.

B. From Methanolysis of 1.—A mixture of compound **1** (1.0 g) and 8 ml of Amberlite IR-120H in 30 ml of methanol was refluxed with stirring for 16 hr. The syrup (0.711 g), obtained after filtration and concentration of the reaction mixture, was applied to a silica gel column (25 g) and eluted with chloroform–methanol (99:1 v/v) and the fractions containing **3** (0.293 g, yield 41%) and **4** (0.084 g, yield 14%) were separated and crystallized as previously described.

Oxetane Ring Cleavage of 1 in Benzene.—A mixture of compound **1** (1.6 g) and 10 ml of Amberlite IR-120H (benzene-washed and air-dried) in 35 ml of benzene was refluxed with stirring for 45 hr. After cooling and filtration, the filtrate was evaporated to a syrup which was deacetylated with sodium methoxide (0.1 *N*, 25 ml) at 25° for 3 hr. The solution was deionized with IR-120H and evaporated to a residue. The residue was crystallized from 50 ml of boiling ethyl acetate to give 0.318 g of **4**, yield 33%.

3,7-Anhydro-1-deoxy-2-*O*-ethyl-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (5). A. From Ethanolysis of Deacetylated 1.—Compound **1** (0.76 g) was deacetylated in absolute methanol (25 ml) with 0.1 *N* sodium methoxide (6 ml) at 0° for 16 hr. The reaction mixture gave 0.496 g of syrup **2**, after deionization with Amberlite IR-120H (ethanol-washed and air-dried) followed by filtration and concentration. Compound **2** was then stirred with 4 ml of the resin for 16 hr at 25°. After filtration, the resin was washed with 10 ml of ethanol and the combined filtrate was evaporated to a syrup which was applied to a silica gel column (20 g) and eluted with chloroform–methanol (95:5 v/v) to give 0.123 g of **5**, crystallized from ethyl acetate–hexane: mp 133–135°; $[\alpha]^{25}D$ +26.2° (*c* 0.30, CH_3OH); yield 21%; nmr (D_2O) τ 5.80–6.30 (m, 7, H-3, H-4, H-5, H-6, H-7, and H-8), 6.42 (q, 2, CH_2 of OEt) 8.70 (s, 6, CCH_3), 8.85 (t, 3, CH_3 of OEt).

Anal. Calcd for $C_{11}H_{22}O_6 \cdot {}^1/_4H_2O$: C, 51.82; H, 8.91. Found: C, 51.99; H, 8.79.

Further elution of the column gave 0.16 g of **4** (34%).

B. From Ethanolysis of 1.—A mixture of compound **1** (1.0 g) and 8 ml of Amberlite IR-120H in 25 ml of ethanol was refluxed with stirring for 20 hr. The syrup obtained after filtration and concentration of the reaction mixture was applied to a silica gel column (40 g) and eluted with chloroform–methanol (99:1 v/v) to give 0.277 g of **4** (40%) and 0.766 g of **5** (9%).

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-2-methylene-D-*glycero*-D-*ido*-octitol (9).—Compound **4** (0.20 g) was acetylated in pyridine (10 ml) with acetic anhydride (0.50 ml) at 25° for 15 hr. The reaction mixture was then poured into ice–water (200 ml) and stirred vigorously. The crystalline product was filtered, washed thoroughly with ice–water, air dried, and recrystallized from ethyl acetate–hexane: mp 105–106°; $[\alpha]^{25}D$ +27.6° (*c* 0.60, $CHCl_3$); yield 0.247 g; ν_{max} 1650 cm^{-1} (methylene); nmr ($CDCl_3$) τ 4.40 (t, 1, $J_{4,5} = J_{5,6}$ = 9 Hz, H-5), 4.60 (t, 1, $J_{5,6} = J_{6,7}$ = 9 Hz, H-6), 4.75 (m, 1, H-7), 4.82 (m, 2, H-8), 6.20 (m, 1, H-3), 7.90, 7.96 (12, OAc), 8.22 (s, 3, CCH_3).

Anal. Calcd for $C_{17}H_{24}O_7$: C, 54.83; H, 6.49. Found: C, 54.63; H, 6.79.

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1,2-dideoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (10). A. From Acetylation of 8.—Methylene derivative **4** (0.12 g) was hydrogenated in 20 ml of ethanol with 0.050 g of palladium over charcoal. The completion of the reaction was followed by tlc, irrigated with solvent B, and the disappearance of the unsaturated compound **4** was checked by using aqueous potassium permanganate as spraying agent. The residue which was obtained after filtration and concentration was recrystallized from ethyl acetate–hexane: mp 127–128°; $[\alpha]^{25}D$ +58.2° (*c* 0.50, CH_3OH); yield 0.093 g; nmr (D_2O) τ 6.10–6.82 (m, 7, H-3, H-4, H-5, H-6, H-7, and H-8), 8.20 (m, 1, methine), 8.98 (d, 3, CCH_3), 9.08 (d, 3, CCH_3). Compound **8** (0.10 g) was acetylated in pyridine (5 ml) with acetic anhydride (0.3 ml) at 25° for 16 hr. The reaction mixture was then poured into ice–water (80 ml), the aqueous solution was extracted with chloroform (two 25-ml portions) and washed with sodium bicarbonate solution and water, and the chloroform extract was dried (Na_2SO_4) and evaporated to a syrup. The syrup was dissolved in 8 ml of hot hexane and crystallized at 0° to yield 0.135 g of **10**: mp 54–56°; $[\alpha]^{25}D$ +32.3° (*c* 1.0, $CHCl_3$); nmr ($CDCl_3$) τ 4.76–5.30 (m, 3, H-4, H-5, and H-6), 5.50–6.20 (m, 3, H-7 and H-8), 6.42 (q, 1, H-3), 7.92–8.20 (13, overlapping OAc and methine), 9.06 (t, 6, CCH_3).

B. From Catalytic Hydrogenation of 9.—Compound **9** (0.20 g) was hydrogenated in 10 ml of ethanol using 0.10 g of palladium over charcoal. The completion of the reaction was checked by tlc (irrigated with solvent A and visualized with potassium permanganate spray). After filtration, the filtrate was evaporated to a syrup which was dissolved in 15 ml of hot hexane and crystallized at 0°, yield 0.178 g. The product was identical with **10**.

Anal. Calcd for $C_{17}H_{26}O_9$: C, 54.54; H, 7.00. Found: C, 54.40; H, 7.13.

4,5,6,8-Tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-2-*O*-methyl-D-*glycero*-D-*ido*-octitol (11).—Compound **3** (0.10 g) was acetylated in pyridine (6 ml) with acetic anhydride (0.2 ml) and the product was worked up in the usual way to give 0.121 g of **11**, crystallized from 10 ml of hexane at 0°: mp 79–80°; $[\alpha]^{25}D$ +45.3° (*c* 0.40, $CHCl_3$); nmr ($CDCl_3$) τ 4.40 (t, 1, $J_{4,5} = J_{5,6}$ = 8 Hz, H-5), 4.82 (q, 1, $J_{3,4}$ = 4.5, $J_{4,5}$ = 8 Hz, H-4), 5.10 (t, 1, $J_{5,6} = J_{6,7}$ = 8 Hz, H-6), 5.50–6.05 (m, 3, H-7 and H-8), 6.18 (d, 1, $J_{3,4}$ = 4.5 Hz, H-3), 6.72 (s, 3, methoxy), 7.96–8.0 (12, Ac), 8.75 (s, 6, CCH_3).

Anal. Calcd for $C_{18}H_{28}O_{10}$: C, 53.43; H, 6.98. Found: C, 53.63; H, 7.02.

3,7-Anhydro-2,4:6,8-di-*O*-benzylidene-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (6).—Compound **2** (0.75 g) was treated with benzaldehyde in the presence of zinc chloride (1.0 g) at 25° for 16 hr. The reaction mixture was poured into ice–water (300 ml) and stirred vigorously after 100 ml of hexane was added. The solid was filtered, washed with ice–water (100 ml), and air dried to give 0.67 g of **6**, recrystallized from ethyl acetate–hexane: mp 221–222°; $[\alpha]^{25}D$ +75.4° (*c* 0.50, $CHCl_3$).

Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.32; H, 6.58. Found: C, 69.07; H, 6.50.

5-*O*-Acetyl-3,7-anhydro-2,4:6,8-di-*O*-benzylidene-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (7).—Compound **6** (0.71 g) was acetylated in pyridine (8 ml) with acetic anhydride (0.3 ml) at 25°. The reaction mixture was poured into ice–water (200 ml) and the crystalline solid was collected and air dried, yield 0.178 g, and then recrystallized from ethyl acetate–hexane: mp 180–181°; $[\alpha]^{25}D$ +62.3° (*c* 0.70, $CHCl_3$).

Anal. Calcd for $C_{25}H_{28}O_7$: C, 68.18; H, 6.41. Found: C, 67.91; H, 6.49.

Registry No.—**1**, 32970-01-7; **3**, 32970-02-8; **4**, 32970-03-9; **5**, 32970-04-0; **6**, 32970-05-1; **7**, 32970-06-2; **9**, 32970-07-3; **10**, 32970-08-4; **11**, 32970-09-5; acetone, 67-64-1; D-glucal triacetate, 2873-29-2.