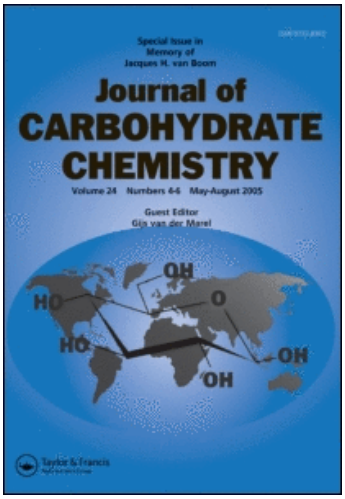

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Friedrich, Klaus and Fraser-Reid, Bert(1994) 'A Route to C2-Methyl-hex-2-enopyranose Synthons', Journal of Carbohydrate Chemistry, 13: 4, 631 — 640
To link to this Article: DOI: 10.1080/07328309408011670
URL: http://dx.doi.org/10.1080/07328309408011670

J. CARBOHYDRATE CHEMISTRY, 13(4), 631-640 (1994)

A ROUTE TO C2-METHYL-HEX-2-ENOPYRANOSE SYNTHONS

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Received July 12, 1993 - Final Form January 26, 1994

ABSTRACT

A synthesis of 4,6-*O*-benzylidene-2,3-dideoxy-2C-methyl-D-*erythro*-1,5-lactone is described. This compound is seen as a general synthon for compounds having 2C-methyl-hex-2-enopyranose skeleta which are required as precursors for intramolecular Diels Alder routes to the AB ring systems of terpenoids. The synthesis begins with the known erythrose derivative obtained by sodium periodate cleavage of 4,6-*O*-benzylidene glucopyranose. Wittig reaction with carbethoxyethylidenetriphenylphosphorane gives the *E*-adduct which, upon irradiation, is isomerized giving a photostationary mixture containing the *E* and *Z* isomers. The latter upon heating is converted into the desired unsaturated aldonolactone.

INTRODUCTION

We have recently described a route to the AB ring system of functionalized terpenoids that involves an intramolecular Diels Alder reaction of hexopyranose derived α,β-unsaturated ketones of type **3**,[1] whose potential for the synthesis of highly functionalized decalines was demonstrated by the preparation of key intermediate **2**, closely related to one in Ziegler's[2] synthesis of Forskolin (**1**). However the strategy was compromised by the rather lengthy route that was required for installing the C2-CH_3 in **5**,[1] since procedures which had been previously successful for hexapyranosides[3] were found to be inapplicable to our

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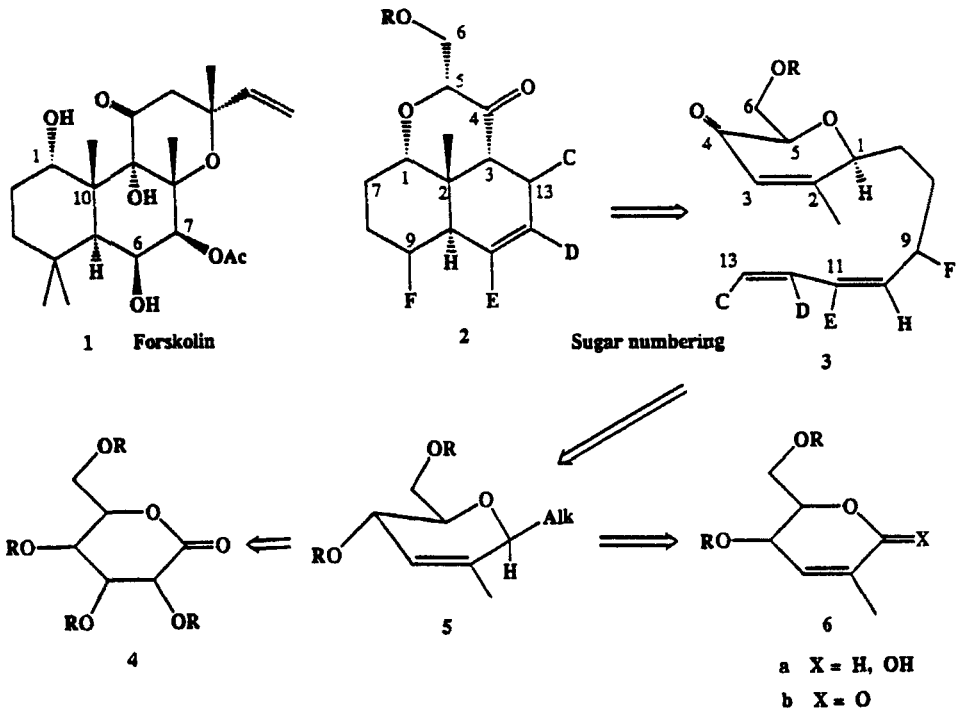


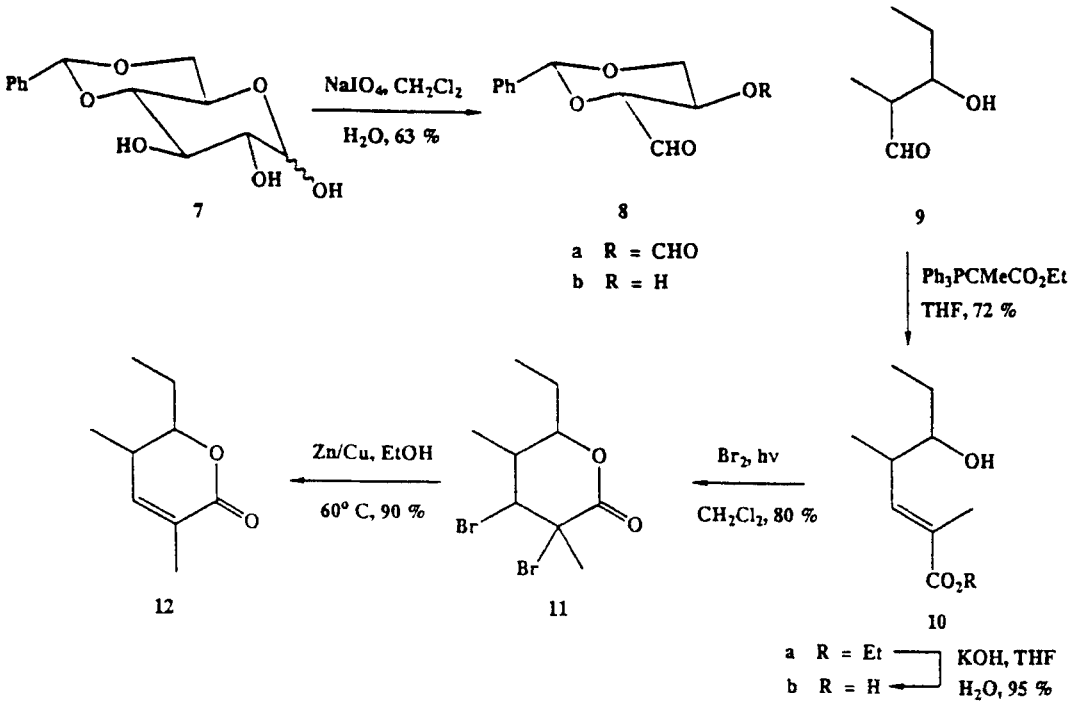
Scheme I

substrates. A more efficient method for installing the C2-CH_3 of **5** would therefore have to be found before the utility of **3** could be examined in greater detail.

An alternative route to **5** (Scheme I) was based on the fact that the aldonolactone **6b** has two of the three chiral centers of **5**. The third, which is an equatorial alkyl residue at C1, had been obtained from the hexonolactone **4** by the well established procedure of Kishi.[4] With this precedent in mind, a derivative of type **6** seemed an attractive precursor to the Intramolecular Diels Alder (IMDA) intermediate **5**. In this article, chemistry related to this concept is presented.

RESULTS AND DISCUSSION

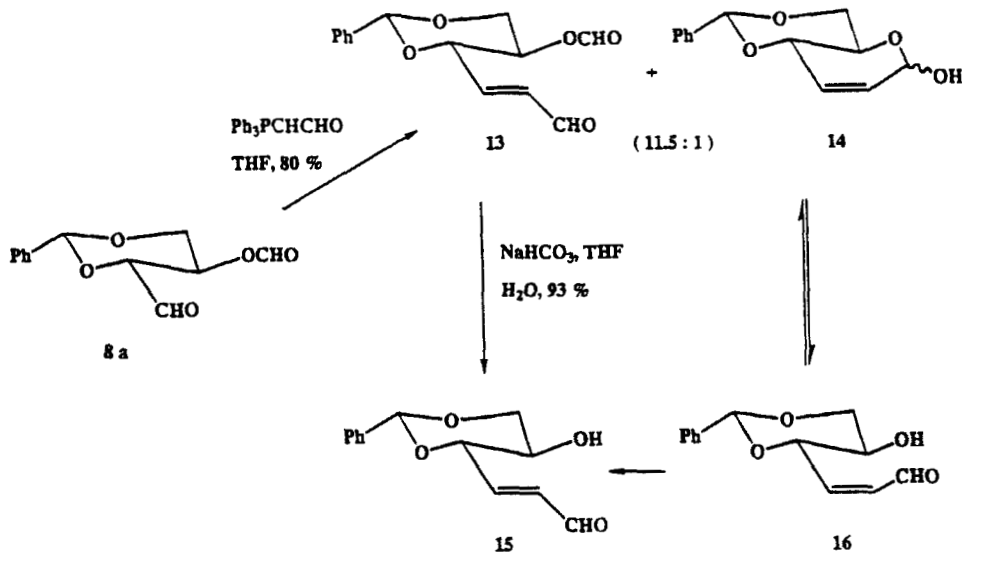
The benzylidene erythrose derivative **8** (Scheme II) which is readily obtained from 4-6-*O*-benzylidene glucose **7**[5] by well known periodate cleavage,[6] was our starting material of choice. Nevertheless it was decided to carry out our preliminary studies on a readily available model, racemic 3-hydroxy-2-



Scheme II

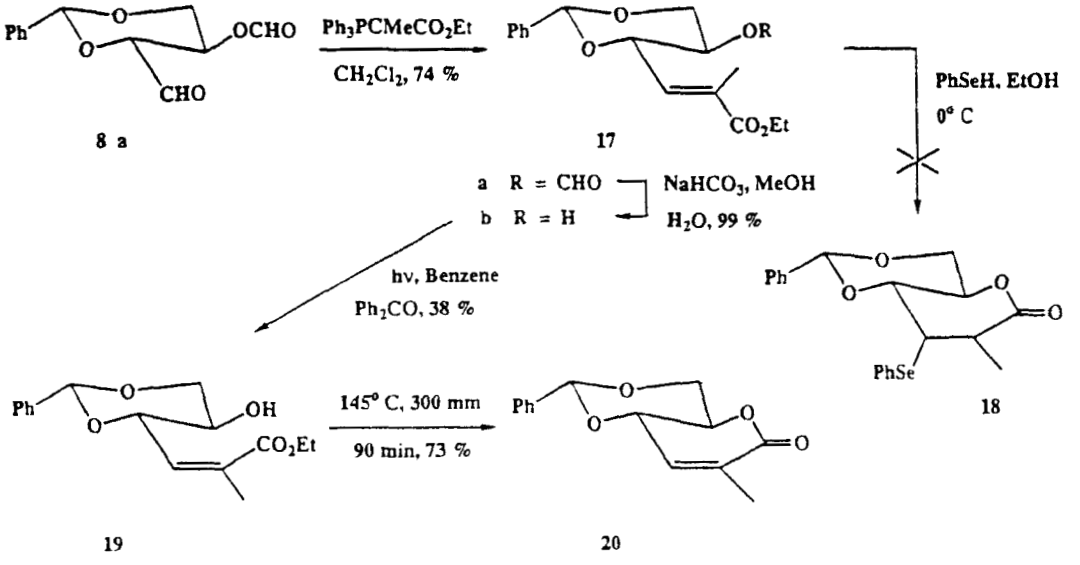
methylpentanal **9**.[7] Reaction with carbethoxyethylidenetriphenylphosphorane in tetrahydrofuran overnight gave compound **10a** as a colorless oil in 72% yield. E-geometry was assigned[8] to this material based on the subsequent transformations which are now described. Thus saponification gave the hydroxy acid **10b** whose failure to form a δ–lactone was taken as evidence of E-geometry. Photochemically induced bromination of the double bond afforded the dibromolactone **11** in excellent yield, and subsequent reductive elimination with zinc-copper couple[9] restored the double bond giving the pyran-2-one **12** as a colorless oil.

We next decided to test the reactivity of compound **8**. Reaction with formyl methylenetriphenylphosphorane at room temperature for three hours gave a 11.5:1 mixture of products assigned as compounds **13** and **14**. The former was recognizable by the presence of two low-field protons, one for the formyl ester, (a singlet at 8.09 ppm), and the other for the aldehydo group (a doublet at 9.60 ppm). Treatment of the material with aqueous sodium bicarbonate led to cleavage of the formyl ester, as consistent with the disappearance of the 8.09 ppm signal. These data as well as the melting point and optical rotation are in agreement with those published for known compound **15**.[10]



Scheme III

Compound **14** was deemed to be an equilibrium mixture of **14** and **16**, the latter being evident from the signal at 9.69 ppm in the ^{1}H NMR spectrum. Furthermore on standing in the laboratory at ambient temperature, **14** was converted into compound **15**. A similar photoisomerization has previously been observed in these laboratories.[11]



Scheme IV

With these model studies completed, the reaction of the erythrose derivative **8a** with carbethoxyethylidenetriphenylphosphorane was examined (Scheme IV). The reaction proceeded smoothly to give the diester **17a**. Treatment with sodium bicarbonate in aqueous methanol chemoselectively cleaved the formyl ester leaving the ethyl ester of compound **17b** in tact. Attempts to effect lactonization of **17b** *via* dibromination, as in the case of compound **10b**, surprisingly led only to recovery of the starting material. Given the earlier success with **10b**, it would appear that the allylic oxygen in **17** must be playing a role. Similarly unsuccessful was an attempt to prepare lactone **18** by conjugate addition of phenylselenol to ester **17b**. In this case the reaction gave intractable material.

Success was achieved by irradiating ester **17b** in benzene in the presence of benzophenone. A photostationary mixture was obtained consisting of compounds **17b** and **19** in 1.4:1 ratio. A variety of experiments with different solvents and sensitizers did not substantially change the composition of the equilibrium mixture.

The isomers were readily separated by column chromatography. Heating of ester **19** to 145° C under reduced pressure for 1.5 hours afforded lactone **20** in 73% as colorless crystals.

Lactone **20** can therefore be obtained from the readily prepared glucose derivative **7** in five simple steps which are all high yielding, including the preparation of **19** even though the precent of conversion is low.

EXPERIMENTAL

General Procedures. Melting points were determined in capillary tubes and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., P.O. Box 2288, Norcross, Georgia 30091. Optical rotations were determined at the sodium D line at the temperatures given with a Perkin-Elmer 241 polarimeter. Proton and carbon magnetic resonance spectra were recorded on a Varian XL-300 spectrometer. Unless otherwise stated, the solvent used was $CDCl_3$ with internal tetramethylsilane or $CHCl_3$ as the standard. Chemical shifts are reported in parts per million (δ). The progress of all reactions was monitored by thin-layer chromatography (TLC), which was performed on aluminum plates precoated with Kieselgel 60 (Merck, 0.2 mm layers) containing fluorescent indicator (Merck, 5554). Detection was by UV light (254 nm) or by dipping in aqueous potassium permanganate solution. Flash chromatography was performed using Kieselgel 60 (230-400 mesh, Merck). Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone ketyl. Petroleum ether had boiling point 35 - 60° C.

Ethyl-2,4-dimethyl-5-hydroxy-2-(E)-heptenoate (10a). 3-Hydroxy-2-methyl-pentanal **9** was prepared from freshly distilled propionaldehyde according to ref. [7] The yield was 42%, bp. 55- 56° C (0.25 mm). To a solution of this material (1.16 g, 10 mmol) in dry THF (100 mL) carbethoxyethylidene-triphenylphosphorane (3.62 g, 10 mmol) was added. The mixture was stirred at room temperature under argon overnight. Evaporation of the solvent and flash chromatography on silica gel (ethyl acetate-petroleum ether 1:4) gave **10a** (1.44 g, 72%) as a colorless oil: TLC R_f = 0.50 (ethyl acetate-petroleum ether 1:4); ^1H NMR (300 MHz, $CDCl_3$) δ 0.85-1.10 (m, 6), 1.28 (t, 3, J = 7.1 Hz), 1.45-1.65 (m, 2), 1.82 (d, 3, J = 1.4 Hz), 2.45-2.60 (m, 1), 3.30-3.45 (m, 1), 4.15 (q, 2, J = 7.1 Hz), 6.63 (m, 1).

(E)-2,4-Dimethyl-5-hydroxy-2-heptenoatic acid (10b). Ester **10a** (0.4 g, 2 mmol) was dissolved in THF (20 mL). Potassium hydroxide (0.16 g, 4 mmol) in water (4 mL) was added and the mixture refluxed under argon for 12 h. After cooling, aqueous citric acid was added and the THF was evaporated. Compound **10b** was extracted into ethyl acetate (3 x 20 mL) and the organic extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent and chromatography on silica gel (ethyl acetate-toluene-*iso*-Pr-OH 1:7:0.5) afforded **10b** (328 mg, 95%) as a colorless oil: TLC R_f = 0.17 (ethyl acetate-toluene-*iso*-Pr-OH = 1:7:0.5); ^1H NMR (300 MHz, $CDCl_3$) δ 0.92-1.10 (m, 6), 1.30-1.50 (m, 1), 1.50-1.65 (m, 1), 1.87 (s, 3), 2.50-2.70 (m, 1), 3.40-3.53 (m, 1), 6.75-6.90 (m, 1); ^{13}C NMR δ 10.5, 12.3, 15.5, 16.7, 27.8, 39.2, 127.1, 146.3, 173.6; m/z 172 (M^+).

2(*H*)-3,4-Dibromo-3,5-dimethyl-6-ethyl-tetrahydropyran-2-one (11). Acid **10b** (0.45 g, 2.61 mmol) was dissolved in dichloromethane (100 mL) and cooled to 0° C. Bromine (0.46 g, 2.87 mmol, 1 M in carbon tetrachloride) was added within 5 min. The solution was allowed to warm up to room temperature and was irradiated with a sunlamp for 30 min. After this time, the color of the solution had turned from red to pale yellow. It was washed with water (30 mL) and dried over $MgSO_4$. Flash chromatography on a short pad of silica gel (ethyl acetate-petroleum ether 1:1) gave dibromide **11** (0.66 g, 80%) as a colorless oil. Even brief storage of the raw material at room temperature would result in the formation of various byproducts: TLC R_f = 0.90 and 0.83 (ethyl acetate-petroleum ether 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, 3, J = 7.8 Hz), 1.38 (d, 3, J = 6.9 Hz), 1.53-1.70 (m, 1), 1.80-1.95 (m, 1), 2.12 (s, 3), 2.30-2.40 (m, 1), 4.20-4.30 (m, 1), 4.42 (d, 1, J = 4.6 Hz); ^{13}C NMR δ 8.6, 11.0, 16.4, 23.3, 30.1, 45.2, 49.7, 81.5, 170.2; m/z 315 (MH^+).

Anal. Calcd for $C_9H_{14}Br_2O_2$: C, 34.43; H, 4.49. Found: C, 34.52; H, 4.52.

2(*H*)-3,5-Dimethyl-6-ethyl-5,6-dihydropyran-2-one (12). The dibromide **11** (0.17 g, 0.54 mmol) was dissolved in absolute ethanol (10 mL) and Zn/Cu[9] (150 mg) was added. The slurry was refluxed for 20 min. After cooling to room temperature, the solution was filtered and the solvent evaporated. Chromatography on silica gel (ether-toluene 1:3) gave lactone **12** (76.4 mg, 90%) as a colorless oil: TLC Rf = 0.63 (ether-toluene 1:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90-1.10 (m, 6), 1.10-1.20 (m, 2), 1.86 (s, 3), 2.2-2.4 (m, 1), 3.40-3.55 (m, 1), 6.50-6.65 (m, 1); ^{13}C NMR δ 9.7, 11.2, 16.9, 24.5, 32.0, 81.6, 127.0, 145.7, 166.0; m/z 155 (MH^+).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.15. Found: C, 70.09; H, 9.21.

2,4-*O*-Benzylidene-3-formyl-D-erythrose (8a). To 4,6-*O*-benzylidene-α-D-glucose (**7**) (1.30 g, 4.8 mmol) in 30 mL of water and 80 mL of dichloromethane was added sodium metaperiodate (2.05 g, 9.6 mmol). The mixture was vigorously stirred for 45 min, then the layers were separated and the aqueous layer extracted twice with 25 mL of dichloromethane. The combined organic extracts were dried over anhydrous $MgSO_4$ and the solvent was evaporated. Compound **8a** was obtained as a colorless crystalline mass (0.72 g, 63%): TLC Rf = 0.45 (toluene-acetic acid-water 70:30:1); mp 89 - 91° C; $[\alpha]_D^{21}$ = +20.1° (c = 0.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (dd, 1, J = 10.4 and 10.2 Hz), 4.28 (dd, 1, J = 10.7 and 1.3 Hz), 4.48 (dd, 1, J = 9.9 and 5.3 Hz), 5.25-5.35 (m, 1), 5.63 (s, 1), 7.30-7.55 (m, 5), 8.07 (s, 1), 9.70 (s, 1); ^{13}C NMR δ 61.3, 67.5, 80.8, 101.2, 126.1, 128.4, 129.6, 136.1, 159.2, 196.4; m/z 237 (MH^+).

(E)-*Aldehydo*-4,6-*O*-benzylidene-2,3-dideoxy-5-formyl-D-*erythro*-hex-2-enose (13) and **4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enose (14).** To a solution of aldehyde **8a** (0.5 g, 2.1 mmol) in THF (25 mL) formyl methylenetriphenylphosphorane (0.7 g, 2.31 mmol) was added. The mixture was stirred at room temperature for 3 h. Evaporation of the solvent and chromatography on silica gel (ethyl acetate-toluene-*iso*-Pr-OH 1:10:1) gave **13** (447 mg, 80%) and **14** (35 mg, 7%). **For 13**: TLC Rf = 0.50 (ethyl acetate-toluene-*iso*-Pr-OH 1:10:1); $[\alpha]_D^{21}$ = -58.8° (c = 1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (dd, 1, J = 10.4 and 10.1 Hz), 4.50 (dd, 1, J = 10.7 and 5.3 Hz), 4.60 (ddd, 1, J = 9.8, 4.8 and 1.3 Hz), 5.00 (m, 1), 5.62 (s, 1), 6.45 (ddd, 1, J = 15.7, 7.8 and 1.4 Hz) 6.82 (dd, 1, J = 15.8 and 4.8 Hz), 7.35-7.60 (m, 5), 8.09 (s, 1), 9.60 (d, 1, J = 7.8 Hz); ^{13}C NMR δ 65.4, 67.8, 77.7, 101.2, 126.1, 128.4, 129.4, 133.2, 136.4, 149.0, 159.2, 192.9; m/z 263 (MH^+).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.20; H, 5.40.

(E)-*Aldehydo*-4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hex-2-enose (15). Formylester **13** (524 mg, 2 mmol) was dissolved in THF (40 mL) and saturated

aqueous sodium bicarbonate solution (10 mL) was added. The mixture was stirred vigorously for 10 h at room temperature. Then aqueous citric acid was added and the THF distilled of under reduced pressure. The product was extracted into ethyl acetate (3 x 25 mL) and the organic layer dried over $MgSO_4$ and evaporated. Chromatography on silica gel (ethyl acetate-toluene-*iso*-Pr-OH 1:10:1) gave **15** (436 mg, 93%) as colorless crystals: mp 120 - 121° C; $[\alpha]_D^{21}$ = -53.3° (c = 0.1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 2.30-2.45 (m, 1), 3.62-3.81 (m, 2), 4.27-4.48 (m, 2), 5.60 (s, 1), 6.49 (ddd, 1, J = 15.8, 7.8 and 1.6 Hz), 7.06 (dd, 1, J = 15.8, 4.2 Hz), 7.30-7.62 (m, 5), 9.61 (d, 1, J = 7.8 Hz); ^{13}C NMR δ 65.1, 71.3, 76.6, 100.9, 126.1, 128.4, 128.5, 129.2, 129.3, 132.1, 136.9, 152.3, 194.0.

(E)-Ethyl-4,6-*O*-benzylidene-2,3-dideoxy-5-*O*-formyl-2C-methyl-D-*erythro*-hex-2-enoate (17a). To a solution of aldehyde **8a** (472 mg, 2 mmol) in dichloromethane (30 mL), Wittig-reagent carbethoxyethylidenetriphenylphosphorane (724 mg, 2 mmol) was added. The mixture was stirred at room temperature for 8 h. After this time, the solvent was evaporated to yield a yellow oil which was purified by chromatography on silica gel with ethyl acetate-petroleum ether 1:2. Ester **17a** was obtained as a colorless oil (476 mg, 74 %) after evaporation of the solvent: TLC Rf = 0.72 (ethyl acetate-petroleum ether 1:2); $[\alpha]_D^{21}$ = +43.0° (c = 2.44 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, 3, J = 7.1 Hz), 1.98 (s, 3), 3.78 (dd, 1, J = 10.5 and 10.2 Hz), 4.20 (qd, 2, J = 7.1 and 2.0 Hz), 4.48 (dd, 1, 10.7 and 5.3 Hz), 4.69 (dd, 1, J = 9.0 and 9.0 Hz), 4.97-5.09 (m, 1), 5.62 (s, 1), 6.69 (dd, 1, J = 8.4 and 1.4 Hz), 7.33-7.56 (m, 5), 8.01 (s, 1); ^{13}C NMR δ 13.8, 14.1, 61.0, 65.7, 67.8, 75.8, 101.2, 126.1, 128.3, 129.3, 133.3, 134.7, 136.7, 159.2, 167.1; m/z 321 (MH^+).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.76; H, 6.29. Found: C, 63.67; H, 6.31.

(E)-4,6-*O*-benzylidene-2,3-dideoxy-2C-methyl-D-*erythro*-hex-2-enoic acid (17b). The formyl ester **17a** (330 mg, 1,1 mmol) was dissolved in methanol (20 mL) and sodium bicarbonate (2.1 mL, 1 n in water) and water (10 mL) were added. The reaction mixture was stirred at room temperature for 1 h. The methanol was distilled off under vacuo and the aqueous layer extracted with ethyl acetate (3 x 10 mL) after been acidified with citric acid in water. The organic extracts were dried over $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel with ethyl acetate-petroleum ether 1:2 to yield **17b** (318 mg, 99%) as a colorless oil, which crystallized upon cooling: TLC Rf = 0.46 (ethyl acetate-petroleum ether 1:2); mp 48° C; $[\alpha]_D^{21}$ = -138.8° (c = 1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 3, J = 7.1 Hz), 2.00 (s, 3), 2.15-2.40 (br, 1), 3.64-

3.82 (m, 2), 4.22 (qd, 2, J = 7.1 and 2.0 Hz), 4.30-4.40 (m, 1), 4.45 (dd, 1, J = 8.5 and 8.5 Hz), 5.58 (s, 1), 6.69 (dd, 1, J = 8.4 and 1.4 Hz), 7.33-7.59 (m, 5); ^{13}C NMR δ 13.8, 14.1, 61.0, 65.3, 70.7, 78.9, 100.9, 126.1, 128.2, 129.0, 133.2, 136.1, 137.2, 167.6; m/z 293 (MH^+).

Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.75; H, 6.89. Found: C, 65.87; H, 6.96.

(Z)-Ethyl-4,6-*O*-benzylidene-2,3-dideoxy-2C-methyl-D-*erythro*-hex-2-enoate (19). The above (*E*)-ethyl ester **17b** (50.3 mg, 0.17 mmol) and benzophenone (2 mg) were dissolved in benzene (8 mL) and irradiated with a UV-lamp (Hanovia PC 201050) for 15 h at room temperature. The solvent was evaporated and the product purified by chromatography on silica gel (ethyl acetate-petroleum ether 1:3) to give the corresponding (*Z*)-ethyl ester **19** (19.3 mg, 38%) as a colorless oil together with **17b** (26.4 mg, 52 %): TLC R_f = 0.41 (ethyl acetate:petroleum ether 1:3); $[\alpha]_D^{21}$ = -12.8° (c = 0.352 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (t, 3, J = 7.5 Hz), 2.02 (s, 3), 3.56-3.72 (m, 2), 4.08-4.45 (m, 4), 4.93 (dd, 1, 8.5 and 8.4 Hz), 5.54 (s, 1), 6.06 (dd, 1, J = 8.1 and 1.5 Hz), 7.25-7.55 (m, H); ^{13}C NMR δ 14.1, 20.1, 61.7, 65.7, 72.1, 76.6, 100.8, 126.1, 128.3, 129.0, 131.4, 137.4, 139.1, 169.4; m/z 247 ($M\text{-}EtOH^+$).

Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.75; H, 6.89. Found: C, 65.64; H, 6.89.

4,6-*O*-Benzylidene-2,3-dideoxy-2C-methyl-D-*erythro*-1,5-lactone (20). Ethyl ester **19** (87 mg, 0.3 mmol) was heated to 145° C under reduced pressure (0.30 mm) for 90 min. in a Kugelrohr apparatus. After this time, the material turned brown and ethanol distilled off. The product was purified by chromatography on silica gel with ethyl acetate-petroleum ether 1:3 to yield lactone **20** (54 mg, 73 %) as colorless crystals: TLC R_f = 0.57 (acetate-petroleum ether 1:3); mp 161 - 162° C; $[\alpha]_D^{20}$ = + 27.0° (c = 1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3), 3.96 (dd, 1, J = 9.7 and 9.4 Hz), 4.25-4.55 (m, 3), 5.61 (s, 1), 6.7 (s, br, 1), 7.35-7.55 (m, 5); ^{13}C NMR δ 17.3, 72.5, 74.0, 78.2, 102.4, 125.7, 128.5, 128.8, 129.9, 136.4, 141.0, 163.7; m/z 247(MH+).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.29; H 5.73. Found: C, 68.35; H, 5.79.

ACKNOWLEDGMENT

K.F. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship. Support by the National Science Foundation (CHE 8920033) is gratefully acknowledged.

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