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Note

# Reinvestigation of the mercuration–demercuration reaction on alkylated glycals: an improved method for the preparation of 2,3-dideoxy-α,β-unsaturated carbohydrate enals ☆

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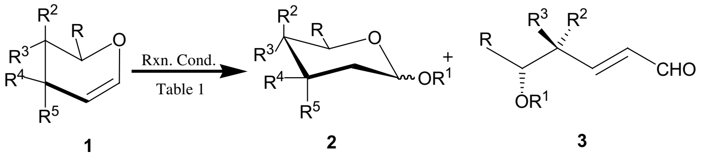
**Abstract**—Alkyl protected glycals can be easily converted into their corresponding α,β-unsaturated enals (Perlin aldehydes) in good to very good yields by reaction with $HgSO_4$ and aqueous 0.02 N $H_2SO_4$ in THF or 1,4-dioxane. While the formation of Perlin aldehydes from benzyl-protected glucal and arabinal was accomplished by refluxing the reaction mixture in 1,4-dioxane, the benzyl-protected galactal and methyl-protected glucal, galactal, and arabinal yielded aldehydes from this reaction at room temperature using THF or 1,4-dioxane as solvent.

*Keywords*: Glycals; $HgSO_4$; Aqueous $H_2SO_4$; THF; 1,4-Dioxane; Perlin aldehyde

α,β-Unsaturated sugar aldehydes (Perlin aldehydes, **3**) have proven to be important precursors for synthesis of biologically potent chemical entities.[1–10] In our attempt to synthesize certain acyclic, chain-extended higher sugar derivatives, we required (2*E*)-4,6-di-*O*-benzyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**3a**, $R^1 = H$, Scheme 1), which could have been obtained from easily available 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-*deoxy*-D-*ara*-



| | R | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|---|
| **a** | $CH_2OBn$ | Ac | H | OBn | OBn | H |
| **b** | $CH_2OBn$ | Ac | OBn | H | OBn | H |
| **c** | H | Ac | H | OBn | H | OBn |
| **d** | $CH_2OCH_3$ | H | H | $OCH_3$ | $OCH_3$ | H |
| **e** | $CH_2OCH_3$ | H | $OCH_3$ | H | $OCH_3$ | H |
| **f** | H | H | H | $OCH_3$ | H | $OCH_3$ |

**Scheme 1.**

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**Table 1.** Results of mercuration–demercuration on benzylated and methylated glycals

| Entry | Solvent | Rxn. temp. (°C) | Rxn. time (h) | Substrate | Product | Yield (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | **2** | **3** |
| 1 | THF | Rt | 96 | **1a** | **2a** and **3a** | Rxn. incomplete | |
| 2 | 1,4-Dioxane | Rt | 96 | **1a** | **2a** and **3a** | Rxn. incomplete | |
| 3[a] | THF | 75 | 6.0 | **1a** | **2a** and **3a** | 52 | 24 |
| 4[a] | 1,4-Dioxane | 110 | 6.0 | **1a** | **2a** and **3a** | 24 | 48 |
| 5 | THF | Rt | 14 | **1b** | **3b** | — | 90 |
| 6 | 1,4-Dioxane | Rt | 8.0 | **1b** | **3b** | — | 90 |
| 7[a] | THF | 75 | 3.0 | **1b** | **2b** and **3b** | 12 | 53 |
| 8[a] | 1,4-Dioxane | 110 | 2.0 | **1b** | **2b** and **3b** | 10 | 58 |
| 9[a] | THF | Rt | 10 | **1c** | **2c** and **3c** | 12 | 48 |
| 10[a] | 1,4-Dioxane | Rt | 3.0 | **1c** | **2c** and **3c** | 15 | 42 |
| 11 | THF | 75 | 2.0 | **1c** | **3c** | — | 75 |
| 12 | 1,4-Dioxane | 110 | 0.75 | **1c** | **3c** | — | 80 |
| 13 | THF | Rt | 10 | **1d** | **3d** | — | 80 |
| 14 | 1,4-Dioxane | Rt | 10 | **1d** | **3d** | — | 82 |
| 15 | THF | Rt | 8.0 | **1e** | **3e** | — | 85 |
| 16 | 1,4-Dioxane | Rt | 8.0 | **1e** | **3e** | — | 88 |
| 17 | THF | Rt | 14 | **1f** | **3f** | — | 60 |
| 18 | 1,4-Dioxane | Rt | 12 | **1f** | **3f** | — | 65 |

[a] Yields calculated after silica gel column chromatography of the acetylated product mixture.

*bino*-hex-1-enitol (3,4,6-tri-*O*-benzyl-D-glucal, **1a**) by its $HgSO_4$-catalyzed hydrolysis with aqueous sulfuric acid in THF following the method reported earlier for the preparation of (2*E*)-4,6-di-*O*-benzyl-2,3-dideoxy-*aldehydo*-D-*threo*-hex-2-enose (**3b**, $R^1 = H$) from 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*lyxo*-hex-1-enitol (**1b**, 3,4,6-tri-*O*-benzyl-D-galactal).[7] Exclusive formation of **3a** ($R^1 = H$) was reported at room temperature in 68 h by $HgSO_4$-catalyzed hydrolysis of 3,4,6-tri-*O*-benzyl-D-glucal (**1a**) in 1,4-dioxane.[8]

Our attempts to obtain **3a** by the reported methods[7,8] proved futile as the reaction failed to go to completion even after continuous stirring for 96 h. The product, isolated in minor quantity from an incomplete reaction mixture by column chromatography, was found to be homogeneous on TLC, but its $^1H$ NMR spectrum confirmed that it was a mixture of two compounds **2a** and **3a** (in both $R^1 = H$).

However, the same reaction was found to give exclusively the desired α,β-unsaturated sugar aldehyde **3b** ($R^1 = H$) from 3,4,6-tri-*O*-benzyl-D-galactal (**1b**) as reported earlier.[7] This prompted us to reinvestigate the $HgSO_4$-catalyzed mercuration–demercuration[†] reaction on benzyl-protected glycals in aqueous acidic medium in THF. We followed the method reported earlier[7] and adopted our own method of performing the reaction at the temperatures specified in Table 1. A THF solution of benzylated glucal **1a** in aqueous acidic medium (0.02 N $H_2SO_4$) was refluxed in presence of a catalytic amount of $HgSO_4$. The crude product on acetylation, followed by column chromatographic purification of the acetylated product mixture, gave **2a** and **3a** in 52% and 24% yield, respectively. By changing the solvent from THF to 1,4-dioxane, which was a solvent of choice for Perlin hydrolysis[12] of 3,4,6-tri-*O*-acetyl-D-glucal, the product distribution was found to be almost reversed (Table 1, entry 4). However, such a solvent effect was not noticed with the benzylated galactal, since only the desired product was obtained in 90% yield when the reaction was carried out at room temperature. On performing this reaction at the refluxing temperature of these solvents, the yield of the desired product **3b** was reduced, and the product was isolated as its acetyl derivative in 53% and 58% yield in THF and 1,4-dioxane, respectively (Table 1, entries 7 and 8).

Thus, the product distribution on Perlin hydrolysis of benzylated glucal **1a** by the above method was found to be solvent dependent, an observation that stimulated us to carry out the same reaction with 3,4-di-*O*-benzyl-D-arabinal (1,5-anhydro-3,4-di-*O*-benzyl-2-D-deoxy-*erythro*-pent-1-enitol) **1c** in THF as well as in 1,4-dioxane at room temperature and also at their refluxing temperatures. It was observed that stirring at room temperature in either solvent yielded an inseparable mixture of **2c** and **3c**[‡] (in both $R^1 = H$, Table 1, entries 9 and 10). The time required for completion of reaction in 1,4-dioxane (3.0 h) was lower than that required in THF (10 h). However, when this reaction was performed at 75 °C in THF (2 h) or 110 °C in 1,4-dioxane (0.75 h), **3c** ($R^1 = H$) was formed almost exclusively ($^1H$ and $^{13}C$ NMR), which could be used as such for further reaction after the usual workup. It is well documented that acyl-pro-

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[†] Mercuration–reductive demercuration of glycals has been reported earlier to give 2-deoxy sugars.[11]

[‡] The formation of **3c** was reported[13] in 24 h when 0.01 N $H_2SO_4$ and 1,4-dioxane were used in the ratio of 10:1.

tected glycals undergo Perlin hydrolysis smoothly at room temperature to yield α,β-unsaturated aldehydes,[12] whereas benzyl-protected glucal or arabinal as observed now did not undergo Perlin hydrolysis at room temperature satisfactorily to give **3a** and **3c** (in both $R^1 = H$), respectively. Besides benzyl-protected glycals, *tert*-butyldiphenylsilyl (TBDPS)-protected glucal, where the TBDPS group is bulkier than the benzyl group, was also included in the present study in order to compare the course of its acid hydrolysis either in THF or 1,4-dioxane with that of benzyl-protected glucal under the same conditions. Therefore, the TBDPS-protected glucal was subjected to Perlin hydrolysis at room temperature, but the desired product was not formed in this case, and the only compound that was isolated from this reaction mixture could be identified as unprotected glucal.

Therefore, in order to ascertain our presumption that size of the alkyl (benzyl or TBDPS) group in the protected glucal and arabinal might be the controlling factor in the Perlin hydrolysis, this reaction was extended to methyl-protected glycals **1d**–**f** in THF as well as in 1,4-dioxane, where the methyl group was much smaller compared to the benzyl or TBDPS group. Here 2,3-dideoxy-α,β-unsaturated carbohydrate enals **3d**–**f** (Scheme 1) were obtained in 60–88% yield by stirring the respective glycals with 10 mol% $HgSO_4$ aqueous acidic medium (0.02 N $H_2SO_4$) in either solvent at room temperature (Table 1, entries 13–18). Thus, based on the above observations, it could be argued that while benzyl- and methyl-protected galactals undergo Perlin hydrolysis smoothly at room temperature resulting only 2,3-dideoxy-α,β-unsaturated aldehydes **3b** and **3e** (in both $R^1 = H$), respectively, in very good yield, the size of the benzyl groups in the benzyl-protected glucal and arabinal do affect the course of their hydrolysis at room temperature, whereas smaller methyl groups in methylated glucal and arabinal (**1d** and **1f**) favored their hydrolysis under the same conditions at room temperature. To our knowledge enals **3d**–**f** are reported here for the first time. The complete physical data and $^1H$ NMR and $^{13}C$ NMR assignment of all the compounds (**2a**–**c**, **3a**–**f**) are provided herein.

In conclusion, a reinvestigation of the hydrolysis of benzyl-protected glucal and arabinal derived from their respective monosaccharides has led to an easy and quicker method of getting α,β-unsaturated sugar aldehydes **3** by refluxing their corresponding benzyl-protected glycals with aqueous sulfuric acid (0.02 N) and a catalytic amount of $HgSO_4$ in 1,4-dioxane. In view of the synthetic utility of α,β-unsaturated sugar aldehydes **3**, this methodology can be exploited for large-scale preparation of such sugar aldehydes from their respective benzylated glycals. However, methyl-protected α,β-unsaturated acyclic sugar aldehydes **3d**–**f** with a free hydroxyl group at C-5 could be easily obtained in very good yield by the above method at room temperature from their respective methyl-protected glycals **1d**–**f**.

## 1. Experimental

### 1.1. General methods

All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates. Visualization was accomplished by warming the plates sprayed with $CeSO_4$ (1% in $2NH_2SO_4$) in an oven at 100 °C. Silica gel (60–120 mesh) was used for column chromatography, and the desired compounds were eluted with an EtOAc–hexane mixture of increasing polarity (5–8%). IR spectra were recorded on a Perkin–Elmer 881 spectrophotometer, and values are expressed in $cm^{-1}$. EI mass spectra were determined on a JEOL-JMS-D-300 spectrometer with an ionization potential of 70 eV. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using argon–xenon (6 kV, 10 mA) as the FAB gas. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Avance 200 MHz instrument for $^1H$ and 50 MHz for $^{13}C$. Chemical shift values are expressed in $\delta$ ppm. Optical rotations were determined on a Rudolph Autopol III polarimeter using a 1-dm cell at 28 °C; concentrations listed are in g/100 mL. Elemental analyses were carried out on Carlo Erba-1108 C, H, and N analyzer.

### 1.2. Typical procedure for preparation of Perlin aldehydes from benzyl- and methyl-protected glycals

To a solution of benzylated glucal **1a** (1.2 mmol) in THF or 1,4-dioxane (5 mL) was added 0.02 N $H_2SO_4$ (10 mL) and a catalytic amount of $HgSO_4$ (10 mol%) in succession. The reaction mixture was stirred at the temperature listed in Table 1. The acid was neutralized with excess barium carbonate, and the suspension was passed through a thick bed of Celite®. The filtrate was extracted three times with small portions of $CH_2Cl_2$. The combined filtrate was washed successively with brine and water, dried over anhydrous $Na_2SO_4$, and evaporated to an oil that was further treated with $Ac_2O$ and dry pyridine at 5 °C. The acetylated crude reaction mixture was worked up by the standard procedure. The syrupy acetate on column chromatographic purification over silica gel afforded **2a** and **3a** as an oil.

The above method was used for the preparation of methyl-protected Perlin aldehydes **3d**–**f** from their respective glycals **1d**–**f**, except that these products were not isolated as their acetate derivatives. These compounds were found to be almost pure ($^1H$ NMR, $^{13}C$ NMR and FABMS spectra) and can be used directly without further chromatographic purification.

### 1.3. Physicochemical and spectral data for compounds 2a–c and 3a–f

**1.3.1. (3*S*,4*S*,5*R*)-3,4,6-Tri-*O*-benzyl-2-deoxy-D-*arabino*-hexopyranose acetate (2a).** IR (neat, cm$^{-1}$): $\nu$ 1694 (C=O), 968, 700; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 7.16–7.32 (m, 30H, Phα and Phβ), 6.24 (d, 1H, $J$ 1.7 Hz, H-1α), 5.65 (dd, 1H, $J$ 11.6 and 2.7 Hz, H-1β), 4.38–4.90 (6d, 12H, $J$ 10.7 Hz, CH$_2$Phα and CH$_2$Phβ), 2.28 (ddd, 2H, $J$ 13.44, 4.8, and 1.38 Hz, H-2′a and H-2′e), 2.03 and 2.09 (2s, 6H, 2×COC*H*$_3$), 1.91 (dd, 2H, $J$ 11.09 and 5.5 Hz, H-2a and H-2e); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 169.7 (*C*OCH$_3$), 138.5, 138.8 (qC of Ph), 128.9, 128.8, 128.4, 128.3, 128.1, 128.0 (Ph), 92.6 (C-1), 78.0 (C-5), 77.3 (C-4), 75.6 (*C*H$_2$Ph) 74.0 (C-3), 72.1 (*C*H$_2$Ph), 69.0 (C-6), 34.7 (C-2), 21.5 (CO*C*H$_3$); FABMS: calcd for $C_{29}H_{32}O_6$, $m/z$ 476; found, $m/z$ 499 (M$^+$+Na). Anal. Calcd for $C_{29}H_{32}O_6$: C, 73.10; H, 6.72. Found: C, 73.37; H, 7.01.

**1.3.2. (3*S*,4*R*,5*R*)-3,4,6-Tri-*O*-benzyl-2-deoxy-D-*lyxo*-hexopyranose acetate (2b).** IR (neat, cm$^{-1}$): $\nu$ 1744 (C=O), 966, 698; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 7.23–7.35 (m, 30H, Phα and Phβ), 6.26 (d, 1H, $J$ 1.9 Hz, H-1α), 5.65 (dd, 1H, $J$ 11.6 and 2.7 Hz, H-1β), 4.36–4.96 (m, 12H, 3×C*H*$_2$Phα,β), 3.87–3.99 and 3.54–3.65 (2m, 10H, H-3α, H-3β, H-4α, H-4β, H-5α, H-5β, H-6α, and H-6β), 2.28 (ddd, 2H, $J$ 13.44, 4.8, and 1.38 Hz, H-2′a and H-2′e), 2.03 and 2.07 (2s, 6H, 2×COC*H*$_3$), 1.91 (dd, 2H, $J$ 11.09 and 5.5 Hz, H-2a and H-2e); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 169.8 (*C*OCH$_3$), 139.1, 138.6, 138.5, 138.3, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.8 (Ph), 92.8 (C-1), 74.4 (C-5), 74.3 (*C*H$_2$Ph), 74.0 (C-4), 72.5 (C-3), 70.8 (*C*H$_2$Ph), 69.3 (C-6), 30.4 (C-2), 21.1 (CO*C*H$_3$); EIMS: calcd for $C_{29}H_{32}O_6$, $m/z$ 476; found, 338 (M$^+$−BnOH−HCHO). Anal. Calcd for $C_{29}H_{32}O_6$: C, 73.10; H, 6.72. Found: C, 73.01; H, 7.03.

**1.3.3. (3*R*,4*S*)-3,4-Di-*O*-benzyl-2-deoxy-D-*erythro*-pentopyranose acetate (2c).** $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 7.25–7.33 (m, 10H, 2×CH$_2$Ph); 6.23 (br s, 1H, H-1), 4.57–4.71 (m, 4H, 2×C*H*$_2$Ph), 4.11–4.23 (m, 1H, H-3), 3.85–3.99 (m, 1H, H-4), 3.74 (m, 2H, H-5a and H-5e), 2.36 (d, 1H, $J$ 14.0 Hz, H-2a), 2.05 (s, 3H, COC*H*$_3$), 1.91 (d, 1H, $J$ 14.2 Hz, H-2e); FABMS: calcd for $C_{21}H_{24}O_5$, $m/z$ 356; found, $m/z$ 355 (M$^+$−1).

**1.3.4. (2*E*,4*S*,5*R*)-5-*O*-Acetyl-4,6-di-*O*-benzyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (3a).** $[\alpha]_D$ +21.7 ($c$ 0.15, CH$_3$OH); IR (neat, cm$^{-1}$): $\nu$ 2810 (CH of CHO), 1700 (C=O), 966, 698; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.64 (d, 1H, $J$ 7.7 Hz, H-1), 7.16–7.32 (m, 10H, 2×CH$_2$*Ph*), 6.72 (dd, 1H, $J$ 15.8 and 6.2 Hz, H-3), 6.30 (dd, 1H, $J$ 15.8 and 7.7 Hz, H-2), 5.17 (q, 1H, $J$ 5.0 Hz, H-5), 4.35–4.65 (m, 4H, 2×C*H*$_2$Ph), 3.75 (m, 1H, H-4), 3.72 (dd, 1H, $J$ 10.6 and 5.2 Hz, H-6a), 3.61 (dd, 1H, $J$ 10.6 and 4.2 Hz, H-6b), 2.03 (s, 3H, COC*H*$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 193.5 (C-1), 170.6 (*C*OCH$_3$), 153.0 (C-3), 134.7 (C-2), 138.1, 137.6, 128.9, 128.5, 128.3, 128.2 (CH$_2$*Ph*), 77.1 (C-5), 73.7 (*C*H$_2$Ph), 73.4 (C-4), 72.4 (*C*H$_2$Ph), 68.0 (C-6), 21.4 (CO*C*H$_3$); FABMS: calcd for $C_{22}H_{24}O_5$, $m/z$ 368; found, $m/z$ 391 (M$^+$+Na). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.73; H, 6.52. Found: C, 70.07; H, 6.97.

**1.3.5. (2*E*,4*R*,5*R*)-5-*O*-Acetyl-4,6-di-*O*-benzyl-2,3-dideoxy-*aldehydo*-D-*threo*-hex-2-enose (3b).** $[\alpha]_D$ +7.5 ($c$ 0.16, CH$_3$OH); IR (neat, cm$^{-1}$): $\nu$ 2815 (CH of CHO), 1742 (C=O), 702; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.53 (d, 1H, $J$ 7.7 Hz, H-1), 7.16–7.32 (m, 10H, 2×CH$_2$*Ph*), 6.69 (dd, 1H, $J$ 15.8 and 6.2 Hz, H-3), 6.34 (dd, 1H, $J$ 15.8 and 7.7 Hz, H-2), 5.19 (q, 1H, $J$ 4.9 Hz, H-5), 4.39–4.66 (m, 4H, 2×C*H*$_2$Ph), 3.75 (m, 1H, H-4), 3.66 (dd, 1H, $J$ 10.6 and 5.2 Hz, H-6a), 3.55 (dd, 1H, $J$ 10.6 and 4.2 Hz, H-6b), 2.06 (s, 3H, COC*H*$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 193.3 (C-1), 170.6 (*C*OCH$_3$), 152.6 (C-3), 134.1 (C-2), 137.9, 137.6, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2 (2×CH$_2$*Ph*), 76.9 (C-5), 73.8 (*C*H$_2$Ph), 73.2 (C-4), 72.8 (*C*H$_2$Ph), 68.2 (C-6), 21.3 (CO*C*H$_3$); FABMS: calcd for $C_{22}H_{24}O_5$, $m/z$ 368; found, $m/z$ 369 (M$^+$+1). Anal. Cacld for $C_{22}H_{24}O_5$: C, 71.73; H, 6.52. Found: C, 71.56; H, 7.01.

**1.3.6. (2*E*,4*S*)-5-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-*aldehydo*-D-*glycero*-pent-2-enose (3c).** $[\alpha]_D$ +30.5 ($c$ 0.14, CH$_3$OH); IR (neat, cm$^{-1}$): $\nu$ 2810 (CH of CHO), 1680 (C=O), 1200 (C–O), 850; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.61 (d, 1H, $J$ 7.6 Hz, H-1), 7.33 (br s, 5H, CH$_2$*Ph*), 6.75 (dd, 1H, $J$ 15.8 and 7.9 Hz, H-3), 6.38 (dd, 1H, $J$ 15.8 and 7.6 Hz, H-2), 4.67 (d, 1H, $J$ 12.0 Hz, C*H*$_2$Ph), 4.53 (d, 1H, $J$ 12.0 Hz, C*H*$_2$Ph), 4.32 (m, 1H, H-4), 4.22 (m, 2H, H-5), 2.06 (s, 3H, COC*H*$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 193.3 (C-1), 170.0 (*C*OCH$_3$), 152.5 (C-3), 137.6 (qC of CH$_2$*Ph*), 134.2 (C-2), 129.0, 128.5, 128.2 (CH$_2$*Ph*), 76.1 (C-5), 72.2 (*C*H$_2$Ph), 65.2 (C-4), 21.2 (CO*C*H$_3$); FABMS: calcd for $C_{14}H_{16}O_4$, $m/z$ 248; found, $m/z$ 249 (M$^+$+1). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.49. Found: C, 66.36; H, 6.76.

**1.3.7. (2*E*,4*S*,5*R*)-4,6-Di-*O*-methyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (3d).** $[\alpha]_D$ +24.0 ($c$ 0.035, CHCl$_3$); IR (neat, cm$^{-1}$): $\nu$ 3435 (O–H), 2930 (=C–H), 1687 (C=O), 1457 (C=C), 1110 (C–O); $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.63 (d, 1H $J$ 7.8 Hz, H-1), 6.85 (dd, 1H, $J$ 15.8 and 5.7 Hz, H-3), 6.32 (dd, 1H, $J$ 15.8 and 7.8 Hz, H-2), 3.95 (t, 1H, $J$ 5.7 Hz, H-4), 3.87 (t, 1H, $J$ 4.5 Hz, H-5), 3.48 (m, 2H, H-6), 3.39 (s, 3H, OCH$_3$), 3.38 (s, 3H, OCH$_3$); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ 193.6 (C-1), 153.8 (C-3), 134.3 (C-2), 81.5 (C-4), 73.1 (C-6), 72.4 (C-5), 59.6 and 58.3 (2×OCH$_3$);

FABMS: calcd for $C_8H_{14}O_4$, *m/z* 174; found, *m/z* 175 ($M^+$+1).

**1.3.8. (2*E*,4*R*,5*R*)-4,6-Di-*O*-methyl-2,3-dideoxy-*aldehydo*-D-*threo*-hex-2-enose (3e).** $[\alpha]_D$ +8.5 (*c* 0.035, $CHCl_3$); IR (neat, $cm^{-1}$): *ν* 3436 (O–H), 2931 (=C–H), 1688 (C=O), 1456 (C=C), 1112 (C–O); $^1H$ NMR (200 MHz, $CDCl_3$): *δ* 9.63 (d, 1H *J* 7.8 Hz, H-1), 6.78 (dd, 1H, *J* 15.8 and 6.0 Hz, H-3), 6.34 (ddd, 1H, *J* 15.8 and 7.7 Hz, 1.1 Hz, H-2), 4.02 (dt, 1H, *J* 5.8 and 1.1 Hz, H-4), 3.81 (m, 1H, H-5), 3.49 (m, 2H, H-6), 3.40 (s, 3H, $OCH_3$), 3.38 (s, 3H, $OCH_3$); $^{13}C$ NMR (50 MHz, $CDC1_3$): *δ* 193.5 (C-1), 153.2 (C-3), 134.3 (C-2), 81.5 (C-4), 73.0 (C-6), 72.5 (C-5), 59.6 and 58.5 (2 × $OCH_3$); FABMS: calcd for $C_8H_{14}O_4$, *m/z* 174; found, *m/z* 175 ($M^+$+1).

**1.3.9. (2*E*,4*S*)-2,3-Dideoxy-4-*O*-methyl-*aldehydo*-D-*glycero*-pent-2-enose (3f).** $[\alpha]_D$ +5.5 (*c* 0.043, $CHC1_3$); IR (neat, $cm^{-1}$): *ν* 3408 (O–H), 2931 (=C–H), 1686 (C=O), 1456 (C=C), 1112 (C–O); $^1H$ NMR (200 MHz, $CDC1_3$): *δ* 9.53 (d, 1H *J* 7.7 Hz, H-1), 6.66 (dd, 1H, *J* 15,8 and 5.6 Hz, H-3), 6.27 (ddd, 1H, *J* 15.8, 7.7, and 1.0 Hz, H-2), 3.97 (m, 1H, H-4), 3.68 (dd, 1H, *J* 11.6 and 3.7 Hz, H-5a), 3.54 (dd, 1H, *J* 11.6 and 6.5 Hz, H-5b), 3.35 (s, 3H, $OCH_3$); $^{13}C$ NMR (50 MHz, $CDC1_3$): *δ* 193.5 (C-1), 153.0 (C-3), 134.2 (C-2), 81.7 (C-4), 64.6 (C-5), 58.1 ($OCH_3$); FABMS: calcd for $C_6H_{10}O_3$, *m/z* 130; found, 131 ($M^+$+1).

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