Synthesis of C1-C6 Segment of Carbonolide B: Wolff Rearrangement of Sugar α-Diazo Ketones

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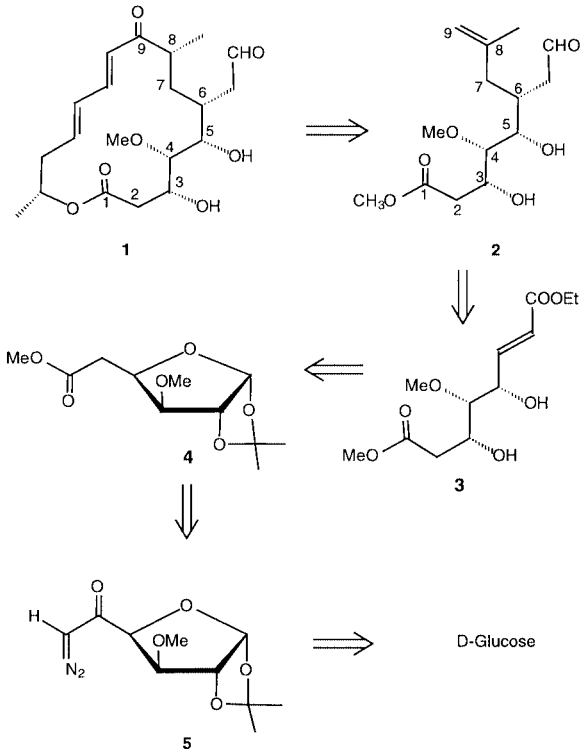
Abstract: Silver benzoate catalysed Wolff rearrangement of a series of α-diazo ketones, derived from furanuronic acids, in methanol proceeds with good yields to produce the corresponding one carbon homologated methyl-5-deoxy-hexo-furanuronate. The utility of methyl-1,2-*O*-isopropylidene-3-*O*-methyl-5-deoxy-α-D-xylo-*hexo*-furanuronate was demonstrated in the synthesis of the right wing segment of carbonolide B - the aglycone of the 16 membered macrolide antibiotic carbomycin B.

Key words: α-diazo ketones, Wolff rearrangement, macrolide antibiotics, carbomycin, carbonolide

Carbomycin B (magnamycin B), tylosin and josamycin (leucomycin A3) constitute the medicinally important 16-membered macrolide antibiotics. The structural aspects, intriguing configurational features, and potential biological properties of these macrolide antibiotics have been the subject of synthetic studies over the years. This has resulted in a number of carbohydrate,[1] as well as non-carbohydrate[2] based convergent syntheses of carbonolide B **1** (the aglycone portion of carbomycin B). Examination of the right hand portion of **1** shows the C1-C9 segment **2** which could be obtained by the Michael addition of lithium methallyl cuprate to the α,β-unsaturated ester **3** (Scheme 1). The key intermediate for the formation of **3** is methyl-α-D-*xylo*-hexo-furanuronate **4a** (upon hydrolysis of 1,2-*O*-isopropylidene functionality followed by Wittig olefination) which represents the C1-C6 carbon framework of **1** and could be derived from D-*glucose*. The presence of three contiguous stereogenic centers from C3 to C5 with hydroxyl functionalities makes the carbohydrate route more appropriate for its synthesis. Only two chiron approaches for **4a** are known so far. The first strategy reported by Nicolaou[3] involves the multi-step synthesis of 5,6-dideoxy-3-*O*-methyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-5-eno-furanose from D-*glucose* followed by hydroboration and oxidative workup with H_2O_2/NaOH to give 5-deoxy-3-*O*-methyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-furanose. Oxidation of the primary alcohol to the acid and esterification with diazomethane afforded **4a**. While, in the second route[4] **4a** (along with its C4 epimer) was derived from the 5,6-dideoxy-6-flouro-6-(*N*-methyl-*N*-phenyl)-5,6-enamino-3-*O*-methyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-furanose by reaction with 5% HCl in methanol. Although, the first route has wide utility, the second approach has very limited synthetic applications. It occurred to us that the Wolff rearrangement of sugar derived α-diazo ketone **5a** in methanol should lead directly to **4a** (free from its C4 epimer) (Scheme 1). The compound **5a** in turn could be readily obtained from D-*glucose*.

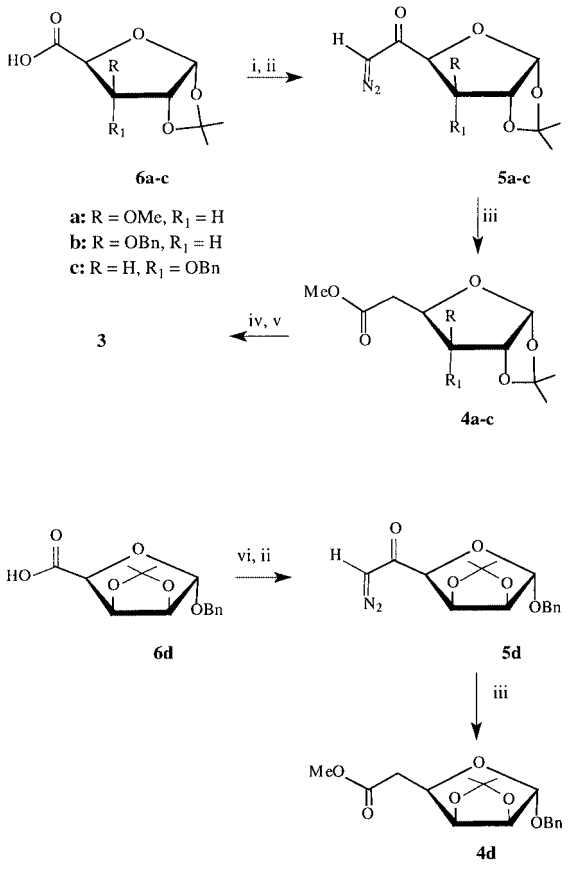


Scheme 1

In recent years, the utility of α-diazocarbonyl derivatives either via carbene generation or through Wolff rearrangement has attracted considerable attention from both the synthetic and the mechanistic point of view.[5] The important synthetic application of the Wolff rearrangement is the Arndt–Eistert synthesis for one carbon homologation of carboxylic acids.[6] The fact that the rearrangement proceeds with the retention of configuration at the asymmetric carbon next to the carbonyl group is advantageous in exploiting the reaction sequence with chiral substrates. Although, this approach has been widely exploited in the syntheses of a number of optically pure compounds,[7] its utility for sugar substrates is highly restricted. To our knowledge, only one unsuccessful report is available[8] wherein, the Wolff rearrangement of 3,4,5,6,7-penta-*O*-

acetyl-1-deoxy-1-diazo-D-*gluco*-heptulose led to the formation of an unsaturated acid namely *trans*-4,5,6,7-tetra-*O*-acetyl-2,3-dideoxy-D-*arabino*-hept-2-enonic acid and not the expected saturated β-acetoxy acid. As a part of our continuing interest in the synthesis of biologically active compounds,[9] we have investigated the Wolff rearrangement of sugar derived α-diazo ketones **5a-d** and our results are reported herein.

The requisite substrates namely furanuronic acids **6a-d** were easily obtained by the usual methods from D-*glucose* and D-*mannose* as reported by us and others earlier.[10] In the initial studies, 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-hexo-furanuronic acid **6a** was converted to the acid chloride by treatment with oxalyl chloride in dichloromethane (Scheme 2). The acid chloride was immediately reacted with diazomethane in diethyl ether to afford the α-diazo ketone **5a**. The relatively unstable **5a** was then subjected to the conditions of Wolff rearrangement using 0.12 molar equivalents of silver benzoate, as the catalyst in the presence of triethylamine in dry methanol. The reaction after six days afforded the expected rearranged product **4a** with retention of configuration at C4 but in low yield (37%). Attempts were made to optimise the reaction conditions by variation in the amounts of silver benzoate. Better results in a short period were obtained with 0.3 molar equivalents of silver benzoate, which resulted in the formation of **4a** in 78% yield. Having synthesized the expected chiral synthon **4a** in good yield, the methodology was extended to the sugar α-diazo ketones **5b** and **5c**, prepared from the **6b** and **6c** respectively, which on Wolff rearrangement led to the corresponding rearranged products **4b** and **4c**. While elaborating the strategy for the D-*mannose* derived α-diazo ketone **5d**; the treatment of oxalyl chloride with α-D-*lyxo*-furanuronic acid **6d,** under our and reported[10] conditions followed by diazomethane gave the methyl ester of α-D-*lyxo*-furanuronic acid in 65% yield along with the expected sugar α-diazo ketone **5d** in low yield (28%). Modification of the reaction conditions using Seebach's procedure[11] wherein **6d** was first reacted with ethyl chloroformate in the presence of Et_3N in THF and then treated with diazomethane in diethyl ether afforded **5d** in good yield. The Wolff rearrangement of **5d**, as stated above, gave **4d** in good yield (Scheme 2).



Reagents and conditions: i) Oxalyl chloride (1.2 equiv), DMF, (1 drop), CH_2Cl_2, 0–25 °C, 3 h; ii) CH_2N_2 (3 equiv), Et_2O, 0–25 °C, 3 h; iii) PhCOOAg (0.3 equiv), Et_3N (6 equiv), MeOH, 0–25 °C, 3 h; iv) TFA/H_2O, 3:2, 0–25 °C, 2 h; v) Ph_3P=CHCOOEt (1.2 equiv), toluene, 16 h, 25 °C; vi) ClCOOEt (1.1 equiv), Et_3N (1.1 equiv), THF, 0 °C, 30 min

Scheme 2

As shown in Scheme 1, compound **4a** contains the appropriate functionalities along with the required stereochemistry of the hydroxyl groups for elaboration to the C1-C9 segment of the carbonolide B. Thus, hydrolysis of the 1,2-*O*-isopropylidene functionality of **4a** with TFA:H_2O followed by Wittig olefination with triphenyl ethoxycarbonylmethylene phosphorane in toluene gave the required α,β-unsaturated ester **3** in 80% yield. The ^{1}H NMR spectra and analytical data of **3** was in consonance with the data reported in the literature.[3]

In conclusion, the Wolff rearrangement of α-diazo ketones **5a-d** is a mild and convenient method for the synthesis of one carbon homologated esters **4a-d**. The utility of **4a** was demonstrated in the synthesis of the right wing portion of carbonolide B, which is of medicinal importance. The easy availability of furanuronic acids in gram scale from the corresponding monosaccharide units makes this route attractive. The potentiality of **4a-d** was also envisioned in the synthesis of rare sugars. For example, 2-deoxy-L-sugars could be easily obtained by the cleavage of 1,2-*O*-isopropylidene functionality followed by $NaBH_4$ reduction. Further applications in this direction and structurally diverse natural products are in progress.

^{1}H NMR spectra of $CDCl_3$ solutions were recorded with a Bruker AMX 500 MHz and a Varian VXR 300S MHz spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS. IR spectra were recorded with a Perkin–Elmer 1600 FT/IR spectrophotometer. Optical rotations were measured at 25 °C with a Perkin–Elmer 241 polarimeter. Analyses (C, H) were performed on a Hosli carbon-hydrogen analyser. Mps were measured on a Thomas–Hoover capillary melting point apparatus and are uncorrected. All the reactions were conducted in oven-dried glassware under dry N_2. TLC was carried out on Polygram Sil G/UV 254 precoated plastic sheets and column chromatography was carried out using silica gel (100–200 mesh) with petroleum ether (bp 60–80 °C)/EtOAc as eluent. Silver

benzoate was prepared as reported.[12] Toluene, CH_2Cl_2, MeOH, THF and Et_2O were dried according to standard procedures. The required α-D-*xylo*-furanuronic acids **6a-c** and α-D-*lyxo*-furonuronic acid **6d** were prepared according to our previous report.[10]

1,2-*O*-Isopropylidene-3-*O*-methyl-6-deoxy-6-diazo-α-D-*xylo*-hexo-furan-5-ulose (5a); Typical Procedure

To a stirred and cooled (0 °C) solution of α-D-*xylo*-furanuronic acid **6a** (1 g, 4.5 mmol) in anhyd CH_2Cl_2 (15 mL) was added oxalyl chloride (0.48 mL, 5.5 mmol) and DMF (0.02 mL) under N_2 atm. The mixture was allowed to attain r.t. (25 °C) and stirred for 3 h. The solvent was removed under reduced pressure and the acyl chloride thus obtained was used in the next step. A solution of acyl chloride in anhyd Et_2O (10 mL) was cooled to 0 °C. To this an ice-cooled solution of diazomethane (18 mmol) in Et_2O (25 mL) was added dropwise. The mixture was stirred for 2 h during which the temperature slowly attained r.t. (30 °C). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to give **5a** as a solid. Yield: 0.84 g, 76%; mp 141–142 °C; $[\alpha]_D^{25}$ –173.63 (*c* 1, $CHCl_3$).

IR (nujol): ν = 2126 (CHN_2), 1620 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CHCl_3$): δ = 1.33 (s, 3H, C*H*$_3$), 1.48 (s, 3H, C*H*$_3$), 3.40 (s, 3H, OC*H*$_3$), 4.08 (d, 1H, *J* = 3.6 Hz, C3-*H*), 4.58 (d, 1H, *J* = 3.7 Hz, C2-*H*), 4.68 (br d, 1H, *J* = 3.6 Hz, C4-*H*), 5.81 (br s, 1H, C*H*N_2), 5.99 (d, 1H, *J* = 3.7 Hz, C1-*H*).

Anal: $C_{10}H_{14}N_2O_5$ (242.23): Calc C, 49.58; H, 5.83. Found C, 49.70; H, 5.85.

1,2-*O*-Isopropylidene-3-*O*-benzyl-6-deoxy-6-diazo-α-D-*xylo*-hexo-furan-5-ulose (5b)

White solid; yield: 0.91 g, 84%; mp 84–86 °C; $[\alpha]_D^{25}$ –153.0 (*c* 1, $CHCl_3$).

IR (nujol): ν = 2117 (CHN_2), 1616 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CHCl_3$): δ = 1.31 (s, 3H, C*H*$_3$), 1.47 (s, 3H, C*H*$_3$), 4.33 (d, 1H, *J* = 3.3 Hz, C3-*H*), 4.57 (d, 1H, *J* = 3.3 Hz, C2-*H*), 4.58 (s, 2H, OC*H*$_2$Ph), 4.72 (br d, 1H, *J* = 3.3 Hz, C4-*H*), 5.84 (br s, 1H, C*H*N_2), 6.01 (d, 1H, *J* = 3.3 Hz, C1-*H*), 7.25–7.37 (m, 5H, Ar-*H*).

Anal: $C_{16}H_{18}N_2O_5$ (318.32): Calc C, 60.37; H, 5.70. Found C, 60.34; H, 5.62.

1,2-*O*-Isopropylidene-3-*O*-benzyl-6-deoxy-6-diazo-α-D-*ribo*-hexo-furan-5-ulose (5c)

White solid; yield: 0.86 g, 79%; mp 120–122 °C; $[\alpha]_D^{25}$ +78 (*c* 1, $CHCl_3$).

IR (nujol): ν = 2117 (CHN_2), 1626 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CHCl_3$): δ = 1.37 (s, 3H, C*H*$_3$), 1.60 (s, 3H, C*H*$_3$), 3.84 (dd, 1H, *J* = 8.7, 3.9 Hz, C3-*H*), 4.50 (br d, 1H, *J* = 8.7, C4-*H*), 4.56 (dd, 1H, *J* = 3.4, 3.9, C2-*H*), 4.70 (d, 1H, *J* = 12.3 Hz, OC*H*$_2$Ph), 4.80 (d, 1H, *J* = 12.3 Hz, OC*H*$_2$Ph), 5.63 (br s, 1H, C*H*N_2), 5.79 (d, 1H, *J* = 3.4 Hz, C1-*H*), 7.25–7.45 (5H, m, Ar-*H*).

Anal: $C_{16}H_{18}N_2O_5$ (318.32): Calc C, 60.37; H, 5.70. Found C, 60.64; H, 5.88.

2,3-*O*-Isopropylidene-1-*O*-benzyl-6-deoxy-6-diazo-α-D-*lyxo*-hexo-furano-5-ulose (5d)

To a soln of α-D-l*yxo*-furanuronic acid **6d** (1 g, 3.4 mmol) in anhyd THF (20 mL) at 0 °C was added Et_3N (0.52 mL, 3.75 mmol) and ethyl chloroformate (0.35 mL, 3.75 mmol) under N_2 atm. The mixture was stirred for 30 min and the solvent was removed under reduced pressure. The mixed anhydride thus obtained was directly used in the next step. A solution of mixed anhydride in anhyd Et_2O was cooled to 0 °C under N_2 atm and to this an ice-cooled solution of diazomethane (0.57 g, 13.6 mmol) in Et_2O (20 mL) was added dropwise. The mixture was stirred for 1.5 h during which the temperature slowly rose to r.t. The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc, 15:1) to give **5d** as a **w**hite solid. Yield: 0.90 g, 83%; mp 126–128 °C; $[\alpha]_D^{25}$ –59.46 (*c* 1, $CHCl_3$).

IR (nujol): ν = 2116 (CHN_2), 1621 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.29 (s, 3H, C*H*$_3$), 1.45 (s, 3H, C*H*$_3$), 4.50 (d, 1H, *J* = 12 Hz, OC*H*$_2$Ph), 4.55 (d, 1H, *J* = 4.0 Hz, C2-*H*), 4.66 (d, 1H, *J* = 6.0 Hz, C4-*H*), 4.70 (d, 1H, *J* = 12.0 Hz, OC*H*$_2$Ph), 5.02 (dd, 1H, *J* = 6.0, 4.0 Hz, C3-*H*), 5.19 (s, 1H, C1-*H*), 5.78 (br s, 1H, C*H*N_2), 7.27–7.50 (s, 5H, Ar-*H*).

Anal: $C_{16}H_{18}N_2O_5$ (318.32): Calc C, 60.37; H 5.70. Found C, 60.17; H, 5.85.

5-Deoxy-3-*O*-methyl-1,2-*O*-(1-methylethylidene)-α-D-*xylo* hexofuranuronic Acid Methyl Ester (4a); Typical Procedure

To a solution of α-diazo ketone **5a**(0.75 g, 3.1 mmol) in anhyd MeOH (12 mL) was added dropwise a solution of silver benzoate (150 mg, 0.62 mmol) in Et_3N (1.5 mL) at r.t. (25 °C) under N_2 atm. The mixture was stirred at the same temperature for 2.5 h. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc, 15:1) to give **4a** as a colorless liquid. Yield: 0.59 g, 78%; $[\alpha]_D^{25}$ –70.29 (*c* 1, $CHCl_3$), $[\alpha]_D^{25}$ –46.23 (*c* 1, MeOH), [Lit[3a] –45.89 (*c* 1, MeOH)].

IR (nujol): ν = 1738 (C=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3H, C*H*$_3$), 1.51 (s, 3H, C*H*$_3$), 2.75 (d, 2H, *J* = 7.0 Hz, C*H*$_2$), 3.39 (s, 3H, OC*H*$_3$), 3.70 (s, 3H, OC*H*$_3$), 3.79 (d, 1H, *J* = 3.3 Hz, C3-*H*), 4.56 (dt, 1H, *J* = 7.0, 3.3 Hz C4-*H*), 4.59 (d, 1H, *J* = 4.0 Hz, C2-*H*), 5.87 (d, 1H, *J* = 4.0 Hz, C1-*H*).

Anal: $C_{11}H_{18}O_6$ (246.25): Calc C, 53.65; H, 7.37. Found C, 53.52; H, 7.60.

5-Deoxy-3-*O*-benzyl-1,2-*O*-(1-methylethylidene)-α-D-*xylo*-hexo-furanuronic Acid Methyl Ester (4b)

Colorless liquid; yield: 0.5 g, 66%; $[\alpha]_D^{25}$ –64.59 (*c* 1, $CHCl_3$).

IR (nujol): ν = 1740 (C=O) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.32 (s, 3H, C*H*$_3$), 1.50 (s, 3H, C*H*$_3$), 2.80 (d, 2H, *J* = 7.0 Hz, C*H*$_2$), 3.64 (s, 3H, OC*H*$_3$), 4.01 (d, 1H, *J* = 3.0 Hz, C3-*H*), 4.46 (d, 1H, *J* = 12.0 Hz, OC*H*$_2$Ph), 4.59 (dt, 1H, *J* = 7.0, 3.0 Hz C4-*H*), 4.62 (d, 1H, *J* = 3.5 Hz, C2-*H*), 4.65 (d, 1H, *J* = 12.0 Hz, OC*H*$_2$Ph), 5.90 (d, 1H, *J* = 3.5 Hz, C1-*H*) 7.25–7.37 (m, 5H, Ar-*H*).

Anal: $C_{17}H_{22}O_6$ (322.35): Calc C, 63.34; H, 6.88. Found C, 63.17; H, 6.85.

5-Deoxy-3-*O*-benzyl-1,2-*O*-(1-methylethylidene)-α-D-*ribo*-hexo-furanuronic Acid Methyl Ester (4c)

Colorless liquid; yield: 0.531 g, 70%; $[\alpha]_D^{25}$ +92.44 (*c* 1, $CHCl_3$).

IR (nujol): ν = 1741 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (s, 3H, C*H*$_3$), 1.36 (s, 3H, C*H*$_3$), 2.46 (dd, 1H, *J* = 7.8, 15.1 Hz, C*H*$_2$), 2.68 (dd, 1H, *J* = 3.9, 15.1 Hz, C*H*$_2$), 3.66 (s, 3H, OC*H*$_3$), 4.40 (ddd, 1H, *J* = 3.9, 7.8, 4.4 Hz, C4-*H*), 4.48–4.60 (m, 3H, C2-*H*, C3-*H*, OC*H*$_2$Ph), 4.79 (d, 1H, *J* = 11.7 Hz, OC*H*$_2$Ph), 5.72 (d, 1H, *J* = 3.9 Hz, C1-*H*) 7.29–7.47 (m, 5H, Ar-*H*).

Anal: $C_{17}H_{22}O_6$ (322.35): Calc C, 63.34; H, 6.88. Found C, 63.27; H, 6.70.

5-Deoxy-1-*O*-benzyl-2,3-*O*-(1-methylethylidene)-α-D-*lyxo*-hexo-furanosiduronic Acid Methyl Ester (4d)

Colorless liquid; yield: 0.516 g, 68%; $[\alpha]_D^{25}$ +51.00 (*c* 1, MeOH).

IR (nujol): ν = 1741.1 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.81 (d, 2H, *J* = 6.8 Hz, CH_2), 3.74 (s, 3H, OCH_3), 4.40–4.52 (m, 2H, OCH_2Ph and C4-*H*), 4.66 (d, 1H, *J* = 5.8 Hz, C2-*H*), 4.71 (d, 1H, *J* = 11.7 Hz, OCH_2Ph), 4.79 (dd, 1H, *J* = 5.8, 3.9 Hz C3-*H*), 5.07 (s, 1H, C1-*H*), 7.35 (br s, 5H, Ar-*H*).

Anal: $C_{17}H_{22}O_6$ (322.35): Calc C, 63.34; H, 6.88. Found C,63.45; H, 6.95.

2*(E)* Octenedioic acid, 4*(R)*, 6*(S)*-dihyroxy-5*(R)*-methoxy-1-ethyl- 8-methyl Ester (3)

An ice-cooled solution of TFA/H_2O (2:1, 2 mL) was added to 5-deoxy-3-*O*-methyl-1,2-*O*-(1-methylethylidene)-α-D-*xylo*-hexofuranuronic acid methyl ester (**4a**, 0.5 g, 2.03 mmol) at 0 °C. The solution was allowed to attain r.t. and stirred for 1.5 h. The acid was removed under reduced pressure and the residue obtained was purified by chromatography on silica gel ($CHCl_3$/MeOH, 19:1) to give methyl 5-deoxy-3-*O*-methyl-α-D-xylo-hexo-1,4-furanuronate as a viscous liquid; yield: 0.37 g, 90%. (The ^{1}H NMR spectra showed the presence of methyl ester signal and the absence of 1,2-*O*-isopropylidene functionality). To a solution of methyl 5-deoxy-3-*O*-methyl-α-D-xylo-hexo-1,4-furanuronate (0.37 g, 1.79 mmol) in anhyd toluene (10 mL) was added triphenylethoxycarbonylmethylene phosphorane (0.75 g, 2.15 mmol). The mixture was stirred at r.t. for 16 h. The solvent was evaporated at reduced pressure to give a thick liquid which on column chromatography on silica gel ($CHCl_3$/MeOH, 98:2) gave **3** as a crystalline solid. Yield: 0.39 g, 80%; mp 48–49 °C, [Lit[3] mp 48–49 °C]; $[\alpha]_D^{25}$ –8.50 (*c* 1, MeOH), [Lit[3] $[\alpha]_D^{25}$ –8.74 (*c* 1, MeOH)]. The spectral and analytical data is in agreement with the reported data.[3]

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