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Note

Alternative preparation of methyl 3-amino-2,3,6-trideoxy-α-D-*arabino*-hexopyranoside and chiral intermediates for the synthesis of thienamycin

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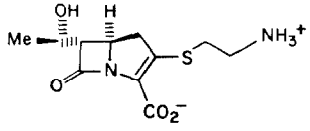
Thienamycin (**1**), obtained from cultures of *Streptomyces cattleya*[1], is an extremely potent, broad-spectrum β-lactam antibiotic possessing a unique chemical structure. The synthesis of thienamycin has been the subject of intense investigation since its discovery and numerous total syntheses have resulted[2]. As only the antipode having the natural configuration displays biological activity, its enantiospecific synthesis remains a desirable synthetic goal, production of **1** by fermentation being of modest efficiency.



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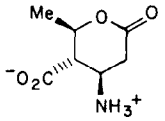

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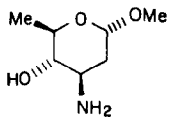

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During the course of investigations directed at preparing the so-called[3] "Melillo lactone" **2** from D-glucose, recent preliminary communications on related approaches by four independent groups[4–7], especially that of Koga *et al.*[6], prompted us to report some useful observations. Herein, we detail an alternative and efficient synthesis of the title compound[6] **3**, an intermediate in the synthesis reported by Koga *et al.*[6]. In addition, our attempt to perform the *C*-homologation **3**→**2** are described.

The readily available[8] 6-bromo-4-benzoate **4** was reduced with W-5 Raney nickel[9] in isopropyl alcohol[10] to afford the 2,6-dideoxy-4-benzoate **5** in quantitative yield (Scheme 1). Although a similar series of transformations to provide the corresponding dibenzoate and diol of **6** has been reported[10,11], our procedure cleanly affords the mono-protected 4-benzoate. Use of such other solvents as methanol or ethanol for reduction by Raney nickel cause scrambling to give a mixture of 3- and 4-benzoates and some diol. The use of W-5 Raney nickel proved superior to other reduction catalysts and the previously reported reductions by tributyltin hydride.

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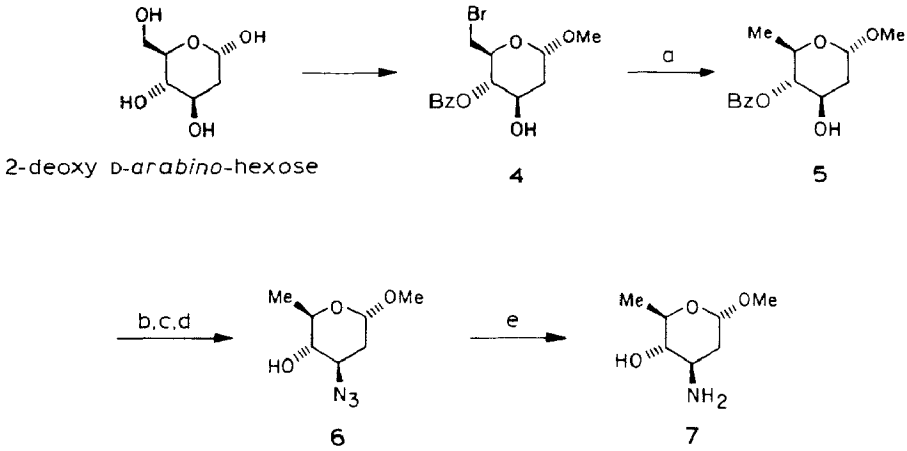
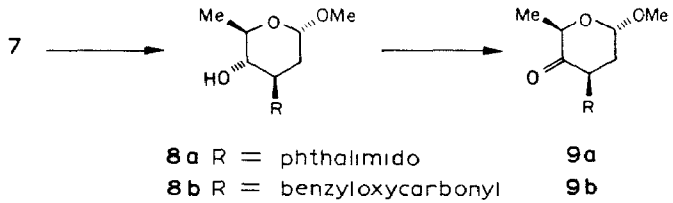


Scheme 1 (*a*) H_2, W-5 Raney Ni, *iso*-PrOH; (*b*) MsCl, Et_3N, THF, 0°, (*c*) NaOMe, MeOH, 25°, (*d*) NaN_3, NH_4Cl, reflux; (*e*) H_2, PtO_2, THF, 25°.

Transformation of **5** into the known* azido alcohol **6** was convniently achieved in the three following steps in 60% overall yield without the isolation of intermediates: (*1*) mesylation of **5**; (*2*) benzoate hydrolysis with concomitant 3,4-epoxide formation; and (*3*) regiospecific opening of the intermediate epoxide with azide. Reduction of the azide **6** to the amino alcohol **7** was efficiently realized by the action of hydrogen–platinum in oxolane (THF) (86%).



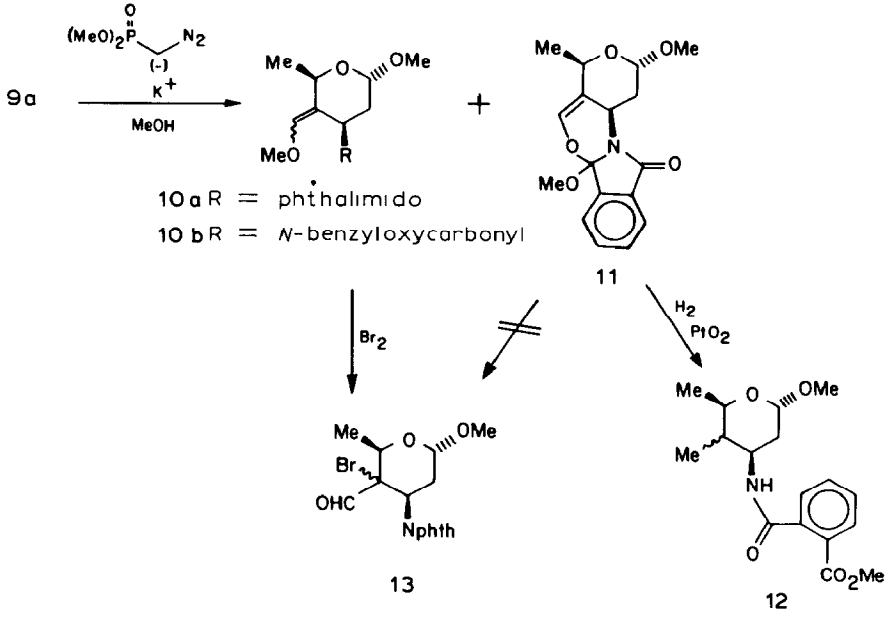
Thus, the amino alcohol **7** is obtained from the bromide **4** in 51% overall yield by a convenient "three-pot" sequence.

Protection of **7** as either the phthalimido derivative **8a** or the *N*-benzyloxycarbonyl derivative **8b** was readily accomplished in the standard manner[13]. Oxidation at C-4 to the ketones **9a** and **9b** was efficiently realized by the Swerm method[14]. Other oxidizing agents, such as pyridinium chlorochromate, give low yields and products that are difficult to purify. The ketone **9b** is a key intermediate in the thienamycin synthesis reported by Koga *et al.*[6], which is *C*-homologated to the methyl enol ether **10b**. We tried a similar approach by using the azido phosphonate

*The enantiomer has been reported[12a], as has methyl 3-azido-2,3,6-trideoxy-β-D-*arabino*-hexopyranoside[12b]; see ref. 4 for comparison of the D series.

reagent of Gilbert and Weerasooriya[15]. In our hands, this was the only reagent that reacted with the apparently very hindered C-4 carbonyl group.

Treatment of **9a** with the potassium salt of dimethyl diazomethylphosphonate afforded two minor products identified as the desired methyl enol ethers **10a** (Scheme 3). The major product, however, was tentatively assigned the structure **11**, resulting from intramolecular trapping of the diazo intermediate[15]. This assign-



ment is based on the conversion of **11** into the methyl ester **12** [ν_{max}^{NaCl} 3240, 1720, and 1560 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 0.83 (d, 3 H, J 6.8 Hz), 1.1 (d, 3 H, J 6.6 Hz), 1.3–2.2 (m, 3 H), 3.29 (s, 3 H), 3.8 (s, 3 H), 3.4–4.7 (m, 3 H), 5.86 (br. m, 1 H), 7.27–7.5 (m, 3 H), and 7.7–7.8 (m, 1 H)] upon hydrogenolysis; both diastereomers of **10a** were stable under these conditions. Additionally, **10a** rapidly decolorized bromine to produce the aldehydes **13** [^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 9.3 (s, 1 H), 9.75 (s, 1 H); mixture of diastereomers], whereas **11** did not consume bromine. The corresponding benzyloxy *N*-carbonyl ketone **9b** cleanly consumed the phosphonate salt; however, the sole, unidentified product did not exhibit a new OCH_3 resonance in the ^{1}H-n.m.r. spectrum, indicative of exclusive intramolecular trapping of the diazo intermediate by the *N*-benzyloxy carbonyl group.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were obtained with Varian EM-360 (60 MHz), JEOL FX-100 (100 MHz), or Nicolet (360 MHz) spectrometers for solutions in $CDCl_3$, unless otherwise stated. Melting points were recorded on a

Mel-Temp instrument in open capillaries and are uncorrected. I.r. spectra were recorded with a Beckman 4240 spectrophotometer. Mass spectra were determined with a VGMM16F g.l.c.–mass spectrometer. Optical rotations were recorded with a Perkin–Elmer Model 241 automatic polarimeter.

Thin-layer chromatography (t.l.c.) was performed with 0.25-mm E. Merck precoated silica gel glass plates (60 F-254) by using 5% ethanolic phosphomolybdic acid and heat and/or u.v. light as developing agent. Preparative-layer chromatography (p.l.c.) was effected with a Harrison Research Chromatotron using 1.0-, 2.0-, or 4.0-mm layer thickness of silica gel adsorbents. Flash chromatography was performed by using E. Merck silica gel 60 (230–400 mesh).

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions unless otherwise stated. n.m.r. multiplicities are reported by the abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Microanalyses were performed by MHW Laboratories.

The following abbreviations are used throughout this section: THF, oxolane (tetrahydrofuran); EtOH, ethanol; MeOH, methanol; EtOAc, ethyl acetate.

*Methyl 4-O-benzoyl-2,6-dideoxy-α-*D-arabino-*hexopyranoside* (**5**). — The bromo benzoate **4** (13.8 g, 40 mmol) was dissolved in 2-propanol (300 mL) at room temperature. To this solution was added a suspension of Raney nickel W-5 in 2-propanol (7 mL). The mixture was degassed and then stirred vigorously under an atmosphere of H_2 for 12 h at room temperature. The suspension was filtered, and the filtrate concentrated, diluted with $CHCl_3$, and washed twice with H_2O. The organic layer was dried (sodium sulfate) and evaporated to afford 10.6 g of the 2,6-dideoxybenzoate **5** as a glass (100%); $[\alpha]_D^{25}$ +121.5° (CH_2Cl_2); ν_{max}^{NaCl} 3460, 2930, 1740, and 1265 cm^{-1}; ^{1}H-n.m.r. (60 MHz, $CDCl_3$): δ 1.36 (d, 3 H, *J* 6.2 Hz), 1.65–2.60 (m, 2 H), 2.85 (br. s, 1 H), 3.36 (s, 3 H), 3.93 (m, 2 H), 4.82 (m, 2 H), 7.48 (m, 3 H), and 8.00 (m, 2 H).

*Methyl 3-azido-2,3,6-trideoxy-α-*D-arabino-*hexopyranoside* (**6**). — To a stirred solution of the benzoate **5** (5.30 g, 19.9 mmol, 1.0 equiv.) in THF (150 mL) at 0° was added triethylamine (2.15 g, 21.2 mmol, 1.0 equiv.) and a solution of methanesulfonyl chloride (2.67 g, 23.3 mmol, 1.1 equiv.) in THF (2 mL) dropwise. The mixture was stirred for 15 min at 0° and 15 min at 25°, filtered to remove $Et_3N \cdot HCl$, and the solvent evaporated to afford 6.62 g (97%) of the 3-mesylate-4-benzoate derivative as a white crystalline solid that was directly used for the next step without further purification; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 1.30 (d, 3 H, *J* 6 Hz), 1.75–2.70 (m, 2 H), 2.80 (s, 3 H), 3.35 (s, 3 H), 3.80 (m, 1 H), 4.75 (br. s, 1 H), 5.15 (m, 2 H), 7.45 (m, 3 H), and 8.10 (m, 2 H).

To a stirred solution of the crude mesylate (1.61 g, 4.68 mmol, 1.0 equiv.) in MeOH (50 mL) was added powdered sodium methoxide (1.51 g, 28 mmol, 5.7 equiv) portionwise at room temperature. The mixture was stirred for 5 h at room temperature, 2 drops of ethanolic phenolphthalein solution was added, and the mixture was made neutral with 0.5M HCl until a colorless solution persisted. To this solution was added sodium azide (0.91 g, 14 mmol, 2.85 equiv.), ammonium

chloride (0.50 g, 9.3 mmol, 1.9 equiv.), and the mixture was boiled under reflux for 24 h. The solution was then allowed to cool, diluted with H_2O (150 mL), and thoroughly extracted with $CHCl_3$. The combined extracts were dried (sodium sulfate), evaporated, and separated on a column of silica gel (eluted with 50% EtOAc in hexanes) to afford 0.55 g (63%) of pure azido alcohol **6** (oil), $[\alpha]_D^{25}$ +127.5° ($CHCl_3$); [lit.[12] L series −131.8° ($CHCl_3$); lit[4] D series +125° ($CHCl_3$)]; $\nu_{max}^{CHCl_3}$ 3440, 2920, 2100, 1125, and 1045 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 1.30 (d, 3 H, J 6.3 Hz), 1.72 (m, 1 H), 2.12 (m, 1 H), 2.60 (br. s, 1 H, D_2O exchangeable), 3.16 (m, 1 H), 3.34 (s, 3 H), 3.69 (m, 2 H), and 4.74 (br. s, 1 H).

*Methyl 3-amino-2,3,6-trideoxy-α-*D-arabino-*hexopyranoside* (**7**). — A mixture of the azido alcohol **6** (3.93 g, 21 mmol) and PtO_2 (47 mg, 0.21 mmol, 0.01 mol%) in THF (400 mL) was vigorously stirred under hydrogen for 6 h at room temperature. Filtration, evaporation of the solvent, and filtration through a small plug of silica gel (50% MeOH in CH_2Cl_2) afforded 2.92 g (86%) of amino alcohol **7**; m.p. 128.5–129.5° (recryst. Et_2O–MeOH), $[\alpha]_D^{25}$ +142.8° (MeOH) (lit.[12] in L series, −145.1° in MeOH); ν_{max}^{NaCl} 3340, 3110, 2875, 1060, and 1045 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 1.27 (d, 3 H J 6.3 Hz), 1.43–2.17 (m, 5 H), 2.71–3.09 (m, 2 H), 3.60 (s, 3 H), 3.69–3.80 (m, 1 H), and 4.67 (m, 1 H).

*Methyl 3-phthalimido-2,3,6-trideoxy-α-*D-arabino-*hexopyranoside* (**8a**). — The amino alcohol **7** (1.52 g, 9.44 mmol, 1.0 equiv.) and *N*-ethoxycarbonylphthalimide (2.28 g, 10.38 mmol, 1.1 equiv.) were dissolved in toluene (75 mL) and stirred at reflux temperature for 4 h. The mixture was allowed to cool to room temperature, washed with brine, dried (sodium sulfate), concentrated, and separated on silica gel (4-mm Chromatotron p.l.c., eluted with 3:1 hexane–EtOAc) to afford the phthalimide **8a** (2.07 g, 75% as a white solid, m.p. 111–113° (recryst. Et_2O–hexanes), $[\alpha]_D^{25}$ +81.2° ($CHCl_3$); $\nu_{max}^{CHCl_3}$ 3450, 2920, 1740, and 1690 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 1.30 (d, 3 H, J 6 Hz), 1.85 (m, 1 H), 2.60 (m, 1 H), 3.00 (br. s, 1 H, D_2O exchangeable), 3.32 (s, 3 H), 3.84 (m, 3 H), 4.72 (br. s, 1 H), and 7.60 (m, 4 H).

Anal. Calc. for $C_{15}H_{17}NO_5$: C, 61.84; H, 5.88; N, 4.81. Found: C, 61.45; H, 6.02; N, 4.79.

Phthalimido ketone (**9a**). — To a stirred solution of oxalyl chloride (0.99 g, 7.8 mmol, 1.1 equiv.) in CH_2Cl_2 (70 mL) at −78° was added Me_2SO (1.22 g, 15.6 mmol, 2.2 equiv.) dropwise. After stirring the mixture for 15 min at −78°, a solution of the phthalimidoalcohol **8a** (2.07 g, 7.1 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added dropwise and stirring was continued for an additional 30 min at −78°. Triethylamine (3.58 g, 35.5 mmol, 5.0 equiv.) was added and the mixture was stirred for 15 min at −78°, 15 min at room temperature, and the solvent removed under diminished pressure. The residue was triturated with THF, filtered to remove $Et_3N \cdot HCl$, evaporated, and passed through a plug of silica gel (2:1, hexanes–EtOAc) to afford 1.78 g (79%) of the pure ketone **9a**; m.p. 133–135° (recryst. MeOH), $[\alpha]_D^{25}$ +96.4° ($CHCl_3$); $\nu_{max}^{CHCl_3}$ 2960, 1740, 1710, 1365, and 1230 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$); δ 1.37 (d, 3 H, J 6.7 Hz), 2.29 (m, 1 H), 3.02 (m, 1 H),

3.48 (s, 3 H), 4.39 (q, 1 H, *J* 6.7 Hz), 4.96 (br. s, 1 H), 5.28 (dd, 1 H, *J* 13, 7 Hz), and 7.75 (m, 4 H).

Phthalimido enol ethers (**11a**). — To a stirred solution of potassium *tert*-butoxide (280 mg, 2.5 mmol, 2.0 equiv.) in methanol (10 mL) was added a solution of dimethyl diazomethylphosphonate (373 mg, 2.5 mmol, 2.0 equiv.) in methanol (3 mL) at room temperature. After completion of the addition, a solution of the ketone **10a** (360 mg, 1.24 mmol, 1.0 equiv.) in THF (2 mL) was added dropwise. After an initial, mild evolution of N_2, the mixture, stirred for 1.5 h at room temperature, was poured into H_2O and thoroughly extracted with CH_2Cl_2. The combined extracts were dried (sodium sulfate), evaporated, and separated on p.l.c. silica gel (eluted with 25% EtOAc in hexanes) to afford 191 mg (49%) of the major isomer **11a**, 116 mg (30%) of the minor isomers **10a**, and unreacted starting material **9a** (63 mg, 18%) (97% conversion).

The major diastereomer showed $\nu_{max}^{CHCl_3}$ 2960, 1720, 1700, 1260, and 1045 cm^{-1}; *m/z* 317 (0.8), 316 (3.2), and 286 (2.8); ^{1}H-n.m.r. (100 MHz, $CDCl_3$); δ 1.24 (d, 3 H, *J* 6.5 Hz), 1.84 (m, 1 H), 2.22 (m, 1 H), 3.33 (s, 3 H), 3.83 (s, 3 H), 4.41 (q, 1 H, *J* 6.5 Hz), 4.63 (m, 1 H), 4.82 (m, 1 H), 6.29 (m, 1 H), 7.32–7.56 (m, 3 H), and 7.56–7.80 (m, 1 H).

The mixture of minor diastereomers showed ν_{max}^{neat} 2965, 1715, 1700, 1370, and 1190 cm^{-1}; ^{1}H-n.m.r. (60 MHz, $CDCl_3$): δ 1.41 (d, 3 H, *J* 6.5 Hz), 2.17 (m, 2 H), 3.11 (s, 1.5 H), 3.17 (s, 1.5 H), 3.47 (s, 3 H), 3.91–5.21 (m, 3 H), 6.31 (m, 1 H), and 7.61 (m, 4 H).

*Methyl 3-(*N*-benzyloxycarbonylamino)-2,3,6-trideoxy-α-*D-arabino-*hexopyranoside* (**8b**). — To a vigorously stirred solution of the amino alcohol **7** (140 mg, 0.87 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL)/saturated $NaHCO_3$ (5 mL) at 25° was added benzyl chloroformate (223 mg, 1.30 mmol, 1.5 equiv.) dropwise. The mixture was stirred for 30 min, diluted with CH_2Cl_2, poured into H_2O, and thoroughly extracted with CH_2Cl_2. The combined organic extracts were dried (sodium sulfate), evaporated, and separated on a small column of silica gel (eluted with 50% EtOAc–hexanes) to afford 165 mg (64%) of **8b**, m.p. 128–130° (Et_2O–hexanes), $[\alpha]_D^{25}$ +125.5° ($CHCl_3$)[6]; ν_{max}^{neat} 3415, 3320, 2970, 1680, and 1535 cm^{-1}; ^{1}H-n.m.r. (100 MHz, $CDCl_3$): δ 1.38 (d, 3 H, *J* 6.1 Hz), 1.37–1.74 (m, 2 H), 2.03 (m, 1 H), 3.03 (m, 1 H), 3.33 (s, 3 H), 3.46–4.14 (m, 2 H), 4.58–4.90 (m, 2 H), 5.10 (s, 2 H), and 7.34 (s, 5 H).

Benzyloxycarbonyl ketone (**9b**). — To a stirred solution of oxalyl chloride (73.0 mg, 0.57 mmol, 1.1 equiv.) in CH_2Cl_2 (10 mL) at −78° was added Me_2SO (90.0 mg, 1.15 mmol, 2.2 equiv.) dropwise. After stirring the mixture for 15 min at −78°, a solution of alcohol **8b** (154 mg, 0.522 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added dropwise. After 15 min at −78°, triethylamine (0.365 mL, 2.61 mmol, 5.0 equiv.) was added and the resulting mixture was allowed to warm to room temperature, and the solvent was removed under diminished pressure. The residue was triturated with THF, filtered to remove $Et_3N \cdot HCl$, evaporated, diluted with CH_2Cl_2, and washed with H_2O. The organic extract was dried (sodium sulfate) and

evaporated to afford 105 mg (69%) of the ketone **9b**, m.p. 73–75° (Et_2O–hexane), $[\alpha]_D^{25}$ +88.5° ($CHCl_3$); ν_{max}^{neat} 3328, 2920, 1745, 1715, 1700, and 1515 cm^{-1}; ^1H-n.m.r. (100 MHz, $CDCl_3$); δ 1.28 (d, 3 H, J 6.6 Hz), 1.90 (m, 1 H), 2.82 (m, 1 H), 3.44 (s, 3 H), 4.37 (q, 1 H, 6.5 Hz), 4.61–4.93 (m, 2 H), 5.09 (s, 2 H), 5.51 (m, 1 H, NH), and 7.32 (s, 5 H).

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