Synthesis of 1,4-Dideoxy-1,4-imino-D-arabinitol (D-AB1) Through a Divergent Approach

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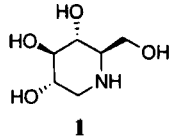
A divergent approach to 2-(hydroxymethyl)pyrrolidine-3,4-diols has been studied with 1,4-dideoxy-1,4-imino-D-arabinitol (D-AB1), a potent glycosidase inhibitor. D-AB1 was efficiently synthesized from 2,3-epoxyalcohol **6a** in overall 11% yield.

Introduction

A variety of mono- and bi-cyclic polyhydroxylated alkaloids are known to be potent glycosidase inhibitors.[1] Recent studies suggest that modification of the polysaccharide and glycoprotein processing in cancer metastasis and viral infections by glycosidase inhibitors might provide new chemotherapies for treatment of such diseases. For example, deoxynorjirimycin (**1**) and castanospermine (**2**) are promising anti-cancer and anti-AIDS compounds, respectively.[2] Several stereoisomers of 2-(hydroxymethyl)pyrrolidine-3,4-diols (**3**) have been reported to be potent glycosidase inhibitors. The D-AB1 (**3a**), (2*R*,3*R*,4*R*)-isomer, is an α-glucosidase inhibitor[3] and potential AIDS-virus replication inhibitor.[1c] Its enantiomer, L-AB1 (**3b**), is a stronger intestinal α-glucosidase inhibitor and powerful anti-AIDS agent.[4,1c]



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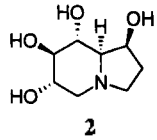

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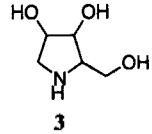
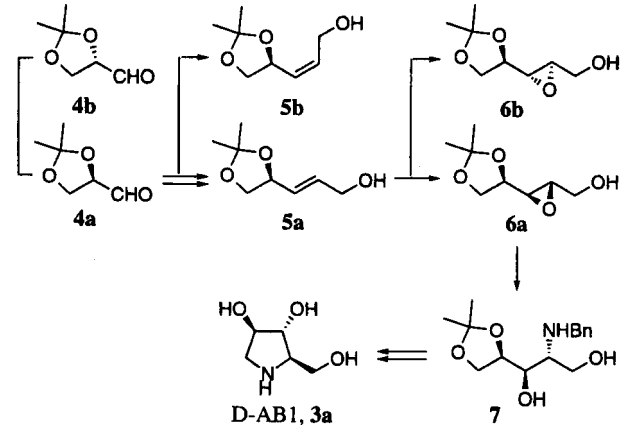


3

Because of the biological interest, much efforts have been made to synthesize pyrrolidines **3**. Most of the stereoisomers of pyrrolidines **3** have been synthesized, mostly from sugar templates[5] and in a few cases by enzymatic aldol reactions.[6] However, all the synthetic procedures could provide only one or few isomers according to the established routes. Development of a divergent approach that is applicable to the synthesis of all stereoisomers of pyrrolidines **3** would be desirable for their biological study. Herein, we report such a divergent synthetic route to one of eight stereoisomers of pyrrolidines **3**, which uses a readily available starting material and well-established reactions. The synthesis involves a C-2 selective opening of epoxyalcohol **6** by an amine equivalent (**6a** → **7**), as depicted in Scheme 1. Since the resulting amine **7** has all the functionality with proper stereochemistry of one of pyrrolidines **3**, its conversion to the corresponding inhibitor (D-AB1) may be a straightforward work. The stereochemical control at C-2 and C-3 of pyrrolidines **3** can be readily made through the Sharpless' asymmetric epoxidation of allylic alcohol **5a** or **5b** (conversion **5** → **6** in Scheme 1).[7] The synthesis of either (*Z*)- or (*E*)-allylic alcohol **5** is also established.[7] Finally, the



Scheme 1.

C-4 stereochemistry of pyrrolidines **3** can be selected either by starting the synthesis from readily available (*R*)- or (*S*)-2,3-*O*-(isopropylidene)glyceraldehyde (**4**).[8] Thus, by selecting a suitable starting material and desired reaction conditions, all stereoisomers of pyrrolidines **3** (eight stereoisomers) could be synthesized according to the route. We have chosen D-AB1 (**3a**) as a representative synthetic target and demonstrate here the validity of our synthetic strategy.

Results and Discussion

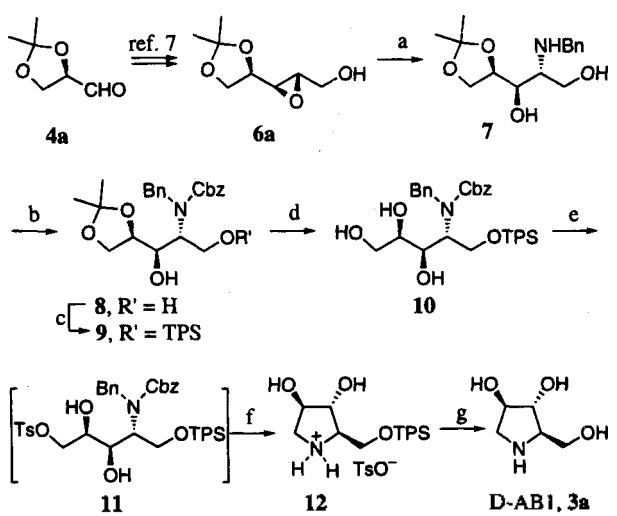
To introduce an amine functionality at C-2 of epoxyalcohol **6**, we decided to use the Kibayashi's aluminum amide procedure, which was previously used in the synthesis of α-homonorjirimycin and castanospermine.[9] In contrast to facile C-3 selective openings of 2,3-epoxyalcohols with amine nucleophiles or their equivalents,[10] there are few methods for the corresponding C-2 openings. In addition to the aluminum amide method, an intramolecular delivery of nitrogen nucleophiles via *N*-benzyl-carbamates is also a useful method for the C-2 openings.[7b,11] The requisite starting epoxyalcohol **6a** was readily synthesized from 2,3-*O*-(isopropylidene)-D-glyceraldehyde (**4a**), according to well-established procedures.[7] Treatment of epoxyalcohol **6a** with a benzylamine-triethylaluminum (1 : 1) complex in dichloromethane at room temperature produced C-2 opened amine **7** as the major product. The regioselectivity of this reaction was > 10 : 1. A minor product, which seemed to be the C-3

opened product, was also observed in a small amount (5-10%). Because removal of this side product was difficult, we carried out the next step without further purification. The amine functionality of **7** was protected with a benzyloxycarbonyl (Cbz) group using benzyl chloroformate in an aqueous bicarbonate-dichloromethane mixture, affording diol **8** in 79% yield. The selective protection of the primary hydroxy group of diol **8** with *tert*-butyldiphenylsilyl chloride (TPSCl) and imidazole in DMF produced monoalcohol **9** in 95% yield. Hydrolysis of the acetonide group of monoalcohol **9** by treatment of 80% aqueous acetic acid produced the corresponding triol **10** in 82% yield. Treatment of triol **10** with *p*-toluenesulfonyl chloride and triethylamine at room temperature produced the desired tosylate **11**, which was sometimes contaminated with unknown products. Hydrogenolysis of the Cbz and benzyl groups of tosylate **11**, followed by *in situ* cyclization with triethylamine afforded silylated pyrrolidinium salt **12** as a white solid with an overall yield of 32%. Finally, deprotection of the silyl group of **12** with 3% methanolic hydrogen chloride containing one drop of 48% hydrofluoric acid, and purification by cation exchange chromatography gave the desired D-AB1 (**3a**) in 85% yield. The final product exhibited a well-resolved ^{1}H NMR spectrum,[12] and showed almost the same specific rotation as the literature value.[5b]

In summary, we have demonstrated that D-AB1 can be synthesized by a convergent route which employs a readily available starting material and well-established reactions. The synthetic route could be equally applied to the syntheses of all other stereoisomers of 2-(hydroxymethyl) pyrrolidine-3,4-diols (**3**), which are potential glycosidase inhibitors.

Experimental

(2*R*,3*R*,4*R*)-2-(*N*-Benzyl)amino-4,5-(isopropylidenedioxy)pentane-1,3-diol (7). To a solution of



Scheme 2. [a] Reaction conditions: (a) $BnNH_2$, Et_3Al, CH_2Cl_2, 25 °C; (b) $ClCO_2Bn$, $NaHCO_3$, CH_2Cl_2-water, 0 °C; (c) $ClSi(^tBu)Ph_2$, imidazole, DMF, 25 °C; (d) AcOH-water, 25 °C; (e) TsCl, Et_3N, CH_2Cl_2, 25 °C; (f) H_2, $Pd(OH)_2$, MeOH, 25 °C; Et_3N, reflux; (g) HCl-MeOH, aq. HF, 25 °C.

benzylamine (0.67 mL, 6.18 mmol) in dichloromethane (20 mL) at 0 °C was added triethylaluminum (6.18 mL, 1.0 M in hexane) dropwise under an argon atmosphere, and the resulting mixture was stirred for 30 min at the same temperature. To this aluminum amide solution was added (2*S*, 3*R*,4*R*)-4,5-isopropylidenedioxy-2,3-oxirane-1-pentanol (**6a**) (1.08 g, 6.18 mmol) in dichloromethane (5 mL), and the reaction mixture was stirred overnight at 25 °C. To the reaction mixture was added 2 N NaOH (10 mL) solution carefully, and the resulting solution was vigorously stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2×15 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate=3/2, v/v) to give **7** in 62% yield (1.08 g), which was contaminated with a small amount of an unknown compound. The unknown was thought to be a C-3 opened isomer, and the amount of which was varied (5-10%) depending on each reaction. **7**: $[\alpha]^{24}_D$-5.19 (*c* 1.08, CH_2Cl_2); IR (neat, cm^{-1}) 3400, 2984, 2907, 1456, 1375, 1254, 1215, 1056; ^{1}H NMR ($CDCl_3$) δ 7.3-7.2 (m, 5H), 4.2-4.1 (m, 1H), 3.98 (dd, *J*=8.22, 6.77 Hz, 1H), 3.8-3.7 (m, 3H), 3.67 (d, *J*=4.80 Hz, 2H), 3.56 (dd, *J*=5.07 Hz, 1H), 2.59 (m, 1H), 2.42-2.01 (br s, 3H), 1.36 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 140.1, 128.4, 128.1, 127.1, 109.3, 76.6, 71.5, 66.5, 60.6, 60.1, 51.4, 26.4, 25.4; MS (EI, *m/z*) 281 (M^+).

(2*R*,3*R*,4*R*)-2-(*N*-Benzyl-*N*-{[(benzyl)oxy]carbonyl})amino-4,5-(isopropylidenedioxy)pentan-1,3-diol (8). To a solution of **7** (1.94 g, 6.90 mmol) in an aqueous dichloromethane solution (water: 17 mL, dichloromethane: 3 mL) at 0 °C were added sodium bicarbonate (1.45 g, 17.3 mmol) and benzyl chloroformate (1.0 mL), sequentially. The resulting mixture was stirred for 2 h at 0 °C before partitioning between dichloromethane (30 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (20 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate=7/3, v/v) to give **8** (2.26 g, 79%): $[\alpha]^{24}_D$-0.15 (*c* 1.1, CH_2Cl_2); IR (neat, cm^{-1}) 3428, 2987, 2939, 1684, 1443, 1375, 1237, 1123, 1059; ^{1}H NMR ($CDCl_3$) δ 7.31-7.24 (m, 10H), 5.17 (m, 2H), 4.71 (d, *J*=15.4 Hz, 1H), 4.42 (d, *J*= 15.4 Hz, 1H), 4.1-3.7 (br m, 7H), 3.5 (br s, 1H), 3.0 (br s, 1H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 157.0, 138.2, 136.1, 128.7, 128.6, 128.3, 128.1, 128.0, 127.7, 109.5, 75.8, 70.4, 67.8, 63.2, 62.6, 52.7, 26.3, 25.3; MS (EI, *m/z*) 415 (M^+).

(2*R*,3*R*,4*R*)-2-(*N*-Benzyl-*N*-{[(benzyl)oxy]carbonyl})amino-1-[(*tert*-butyldiphenylsilyl)oxy]-4,5-(isopropylidenedioxy)pentan-3-ol (9). A DMF (14 mL) solution of diol **4** (3.00 g, 7.21 mmol), imidazole (0.98 g, 14.42 mmol), and *tert*-butyldiphenylsilyl chloride (TPSCl, 2.25 mL, 7.35 mmol) was stirred at 25 °C for 3 h. The mixture was partitioned between diethyl ether (30 mL) and water (20 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: 10 → 20% ethyl acetate in hex-

anes) to give **9** (4.48 g, 95%): $[\alpha]^{24}_D$+13.9 (*c* 0.56, CH_2Cl_2); IR (neat, cm $^{-1}$) 3469, 3068, 2942, 2891, 2857, 1693, 1462, 1427, 1238, 1096; ^{1}H NMR ($CDCl_3$) δ 7.7-7.2 (m, 20H), 5.13 (m, 2H), 4.9-4.4 (m, 2H), 4.1 (m, 2H), 3.9-3.3 (m, 6H), 1.30 (s, 3H), 1.23 (s, 3H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 157.0, 138.3, 136.3, 135.6, 133.3, 129.7, 128.7, 128.5, 128.0, 127.9, 127.7, 127.3, 109.5, 76.3, 72.6, 67.4, 65.7, 62.3, 62.1, 52.7, 26.9, 26.3, 25.3, 19.1; MS (EI, *m/z*) 653 (M^+).

(2*R*,3*R*,4*R*)-4-(*N*-Benzyl-*N*-{[(benzyl)oxy]carbonyl}amino)-5-[(*tert*-butyldiphenylsilyl)oxy]pentan-1,2,3-triol (10). An aqueous acetic acid (1.76 mL, 80% v/v) solution of **9** (461 mg, 0.705 mmol) was stirred at 25 °C until the milky solution became clear (*ca.* 12 h). The reaction mixture was neutralized with a saturated aqueous sodium carbonate solution and was extracted with dichloromethane (3×20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (eluent: 30 → 80% ethyl acetate in hexanes) to give triol **10** (370 mg, 86 %): $[\alpha]^{24}_D$+2.53 (*c* 1.03, CH_2Cl_2); IR (neat, cm $^{-1}$) 3411, 3068, 3031, 2942, 2890, 2867, 1683, 1461, 1426, 1233, 1101; ^{1}H NMR ($CDCl_3$) δ 7.6-7.0 (m, 20H), 5.16 (dd, *J*=20.2, 12.2 Hz, 2H), 4.59 (br s, 2H), 4.13 (br s, 1H), 3.98 (br t, *J*=6.8 Hz, 1H), 3.78 (br s, 1H), 3.59 (br s, 1H), 3.5-3.3 (m, 4H), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 157.5, 137.9, 136.1, 135.6, 133.0, 129.9, 128.7, 128.6, 128.2, 127.9, 127.8, 127.6, 72.5, 70.7, 67.5, 64.1, 62.1, 61.8, 50.8, 26.9, 19.1; MS (EI, *m/z*) 637 (M+Na, 18), 614 (M+H).

(2*R*,3*R*,4*R*)-1,4-Dideoxy-1,4-imino-2-{[(*tert*-butyldiphenylsilyl)oxy]methyl}-D-arabinitol-1-*p*-toluenesulfonic Acid (12). To a solution of **10** (796 mg, 1.25 mmol) in dichloromethane (2.0 mL) at 0 °C were added triethylamine (0.18 mL, 1.30 mmol) and *p*-toluenesulfonyl chloride (248 g, 1.30 mmol), and the mixture was stirred for 1 h at 25 °C. The reaction mixture was partitioned between water (20 mL) and dichloromethane (20 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (2×20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (20% ethyl acetates in hexanes) to give tosylate **11** (742 mg, 77%), which was subjected to the next step without further purification.

To a methanol (4.8 mL) solution of **11** (742 mg, 0.97 mmol) was added $Pd(OH)_2$ (20% on carbon, 52 mg, 10 mol %), and the heterogeneous mixture was stirred under a hydrogen atmosphere (about 60 psi) using a Parr hydrogenator until the reaction was complete (12 h). The reaction mixture was filtered through a filter paper to remove insoluble materials, and the filtered solution was treated with triethylamine (0.40 mL). The resulting mixture was refluxed for 12 h, then the solvent was concentrated by a rotavapor. The residue was diluted with dichloromethane and kept in a refrigerator to give pyrrolidinium tosylate **12** as a white crystal (220 mg, 42% for two steps): mp 195.3-196.8 °C; $[\alpha]^{24}_D$+16.4 (*c* 1.3, CH_3OH); IR (KBr pellet, cm $^{-1}$) 3427, 2959, 2856, 1606, 1471, 1247, 1172, 1113, 1056, 1005; ^{1}H NMR ($CDCl_3$+CD_3OD) δ 7.6-7.1 (three groups of peaks, 14H), 3.9-3.8 (m, 3H), 3.6-3.3 (m, 3H), 2.75 (br s, 4H), 2.27 (s, 3H), 0.98 (s, 9H); ^{13}C NMR ($CDCl_3$+CD_3OD) δ 141.3, 140.4, 135.4, 132.4, 129.9, 128.8, 127.8, 125.7, 74.9, 67.7, 61.9, 51.0, 26.6, 21.1, 19.0; MS (EI, *m/z*) 566 (M+Na), 544 (M^+).

(2*R*,3*R*,4*R*)-1,4-Dideoxy-1,4-imino-D-arabinitol (D-AB1, 3a). The silyl ether **12** (79 mg, 0.145 mmol) was treated with 3% methanolic HCl (0.3 mL) solution and one drop of 48% of hydrofluoric acid, and the mixture was stirred for 12 h at 25 °C. The reaction mixture was concentrated *in vacuo* and the residue was purified by cation-exchange chromatography (Dowex 1×8-100, eluent: MeOH) to give D-AB1 in 85% yield (17 mg): $[\alpha]^{24}_D$+7.3 (*c* 1.38, H_2O); lit.[5b] $[\alpha]^{24}_D$+7.8 (*c* 0.46, H_2O); ^{1}H NMR (D_2O) δ 4.26 (dd, *J*=5.6, 3.8 Hz, 1H), 3.96 (dd, *J*=5.6, 3.8 Hz, 1H), 3.86 (dd, *J*=10.6, 4.4 Hz, 1H), 3.77 (dd, *J*=10.6, 6.2 Hz, 1H), 3.26 (dd, *J*=12.5, 5.6 Hz, 1H), 3.12 (dd, *J*=11.2, 5.6 Hz, 1H), 2.97 (dd, *J*=12.5, 4.4 Hz, 1H); ^{13}C NMR (D_2O+acetone-d_6) δ 79.2, 77.7, 65.7, 62.2, 50.9; MS (EI, *m/z*) 177 (M+CO2), 133 (M^+).

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12. The ^{1}H NMR spectra of other Cbz-protected intermediates exhibited broad peaks due to the hindered nitrogen inversion.

The Preparation of Poly(*N*-methylpyrrole) Bilayers with Entrapped Anthraquinone-2-sulfonate

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Anthraquinone-2-sulfonate (AQS) release from poly(*N*-methylpyrrole anthraquinone-2-sulfonate) (PNMP-AQS) was investigated at open circuit and compared with electrochemically stimulated release during potential cycling. It was found that the fast AQS release from PNMP-AQS single layers is substantially retarded and the amounts of spontaneously and electrochemically releasable AQS can be reduced by constructing bilayers, consisting of PNMP-AQS inner layers and PNMP outer layers. PNMP-Cl outer layers exhibited higher effectiveness for entrapping AQS within inner layers than PNMP/poly(styrene sulfonate). The effects of outer layer thicknesses on AQS release were also examined with PNMP-AQS : PMP-Cl. The electroactivity enhancement of PNMP-AQS : PNMP-Cl bilayers due to entrapped AQS was confirmed by chronocoulometry.

Introduction

Various interesting properties[1] of conducting polymers have been extensively studied since it was reported by Chiang *et al.*[2] that polyacetylene could obtain a 12 order of magnitude increase of conductivity upon oxidative doping. Most of them come from reversible switches of conducting polymers between insulating and conducting states within a certain potential range. During redox switches in electrolyte solutions, conducting polymers incorporate or release ionic species to maintain charge neutrality in a polymer matrix.[3] It is well known that conducting polymer films containing small dopant anions such as poly(pyrrole chloride) balance the charge through anion movements, while cations are mainly involved in ion transport mechanism for ones containing immobile dopant anions such as polypyrrole/poly (styrene sulfonate) (PP/PSS).[4]

These ion transport behaviors can be controlled by constructing bilayers where two electroactive polymer films are physically segregated and no electrical contact exists between the electrode and the outer layer. For example, Reynolds *et al.*[5] addressed that anion dominant transport behaviors of polypyrrole/poly(styrene sulfonate) at higher potential regions can be alleviated through construction of polypyrrole/poly(styrene sulfonate):poly(vinyl ferrocene) bilayers, in which an individual layer sustain its typical ion transport mechanism during redox switching. They also reported that the presence of the outer layer retards the diffusion rate of ionic species, responsible for the inner layer doping-dedoping process.

In this paper, we describe electrochemical behaviors of poly(*N*-methylpyrrole anthraquinone-2-sulfonate) (PNMP-AQS) single layers and bilayers consisting of PNMP-AQS as inner layers and PNMP with various dopant anions as outer layers, in which entrapped AQS can play a role of charging capacity increase of the film as well as a dopant,