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A New Approach to the Stereospecific Synthesis of a Dihydroxyethylene Isostere

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A dihydroxyethylene isostere, (2*S*,3*R*,4*S*)-4-amino-5-cyclohexyl-1-morpholino-2,3-pentanediol, which is a component of non-peptidic, orally active, low-molecular-weight renin inhibitors, was synthesized stereospecifically starting from prochiral divinylcarbinol *via* the Sharpless epoxidation.

Keywords renin inhibitor; dihydroxyethylene isostere; stereospecific synthesis; divinylcarbinol; Sharpless epoxidation; (2*S*,3*R*,4*S*)-4-amino-5-cyclohexyl-1-morpholino-2,3-pentanediol

The renin-angiotensin system plays a central role in the regulation of blood pressure. Renin is a highly specific aspartic protease which generates angiotensin I from angiotensinogen. Angiotensin I is a hemodynamically inactive decapeptide, but it is transformed by the angiotensin-converting enzyme into the octapeptide angiotensin II, which is a very potent vasoconstrictor. Therefore, a large number of human renin inhibitors have been investigated as potential agents of antihypertensive therapy.[1]

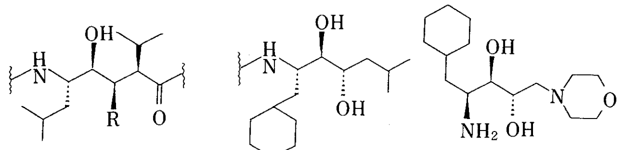
The hydroxyethylene isostere **1a** has been increasingly used as a transition-state analogue.[2] Thaisrivongs *et al.* introduced a hydroxyl group at position 3 of the hydroxyethylene isostere, obtaining the dihydroxyethylene isostere **1b**, but failed to increase the potency.[3] Recently, another type of dihydroxyethylene isostere **2** has been synthesized and it was reported that inhibitors containing **2** showed potent inhibitory activities.[4] More recently, we have reported[5a] a novel renin inhibitor, BW-175, which is a non-peptidic, orally active, low-molecular-weight inhibitor having the dihydroxyethylene isostere, (2*S*,3*R*,4*S*)-4-amino-5-cyclohexyl-1-morpholino-2,3-pentanediol (ACMP, **3**).

We have already synthesized ACMP starting from 1,2:5,6-di-*O*-isopropylidene-D-allofuranose.[5b,c] In this paper we report a new and efficient synthesis of ACMP from the prochiral divinylcarbinol **4** *via* the Sharpless epoxidation.

The synthetic route is outlined in Chart 1. The monoepoxy alcohol **5** is readily obtained in 64% yield with high diastereomeric (98%) and enantiomeric (97%) purity.[6a] The alcohol **5** was protected in tetrahydrofuran (THF) at room temperature as the corresponding benzyl ether **6** (Bn = benzyl)[6b—g] in 96% yield without Payne rearrangement. The regiospecific epoxide opening of **6** with cyclohexylmagnesium chloride in the presence of cuprous iodide[7] followed by mesylation gave **7** in 62% yield from **6**. After the replacement of the mesyloxy group by the azide group, by treatment with sodium azide, oxidation of the double bond with osmium tetroxide proceeded in a diastereoselective fashion[8] (84% de, inseparable) to afford **8** in 88% yield from **7**. The diol **8** was then converted into the epoxide **9** by tosylation followed by treatment with potassium carbonate in methanol in 73% yield. Reaction of **9** with morpholine in ethanol under reflux gave **10** in 98% yield. Hydrogenation of **10** with palladium-black in the presence of di-*tert*-butyl dicarbonate[9] at atmospheric pressure followed by recrystallization gave optically pure Boc-ACMP (**11**) in 76% yield from **10**. The absolute configuration at position 2 of the major oxidation product **8** was found to be *S* by converting **8** into Boc-ACMP and comparing the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the product with that of the authentic compound synthesized from 1,2:5,6-di-*O*-isopropylidene-D-allofuranose.[5b,c] Thus, we have established an efficient stereo-controlled synthesis of the dihydroxyethylene isostere from prochiral material.

Experimental

Melting points were determined with a Yanagimoto melting point

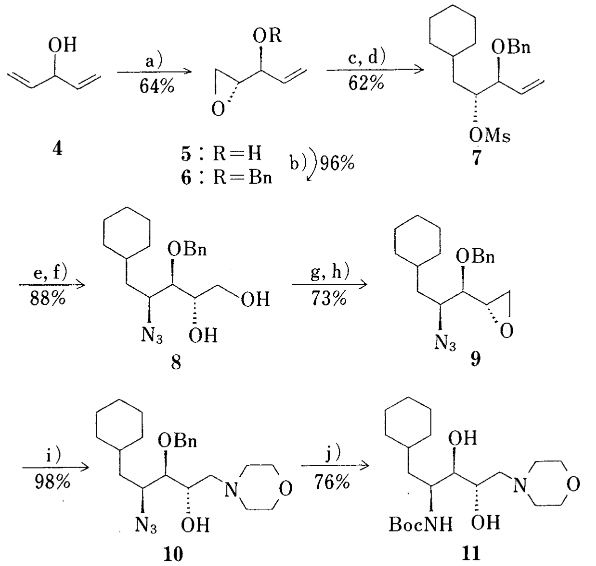


1a : R=H
1b : R=OH

2

3

Fig. 1



a) L-(+)-DET, Ti(*O*-iso-Pr)$_4$, TBHP, CH_2Cl_2 b) BnBr, NaH, *n*-Bu_4NI, THF c) cyclohexylmagnesium chloride, CuI, THF-ether d) Ms-Cl, Et_3N, CH_2Cl_2 e) NaN_3, DMF f) OsO_4, *N*-methylmorpholine *N*-oxide, acetone−H_2O g) Tos-Cl, pyridine h) K_2CO_3, MeOH i) morpholine, EtOH j) H_2/10% Pd-C, Boc_2O, MeOH

Chart 1

apparatus and are uncorrected. Infrared (IR) spectra were measured with a Hitachi 270-30 infrared spectrophotometer. ^{1}H-NMR (300 MHz) spectra and ^{13}C-nuclear magnetic resonance (^{13}C-NMR, 75 MHz) spectra were recorded with a Varian VXR-300 spectrometer in deuteriochloroform ($CDCl_3$), with tetramethylsilane (TMS) as an internal standard. Fast atom bombardment mass spectra (FAB-MS) were obtained with a JEOL JMS-DX 300 mass spectrometer. Optical rotations were determined with a Horiba SEPA-200 high-sensitivity polarimeter. Column chromatography was done on Kieselgel 60 (E. Merck, 70—230 mesh). The organic solutions were dried over $MgSO_4$ before vacuum evaporation.

(2*R*,3*S*)-1,2-Epoxypent-4-en-3-ol (5) Titanium tetraisopropoxide (10.15 g, 36.0 mmol) and L-(+)-diethyl tartrate (8.84 g, 43.0 mmol) were added to a mixture of powdered, activated molecular sieves 3A (7 g) and dry dichloromethane (CH_2Cl_2, 500 ml) at −30 °C. *tert*-Butyl hydroperoxide (40.5 ml, 202 mmol, 5.0 M in CH_2Cl_2, dried over molecular sieves 3A prior to use) was added dropwise, and the resulting mixture was stirred for 10 min. Then divinylcarbinol (10.0 g, 119 mmol, dissolved in 20 ml of CH_2Cl_2) was added over a period of 20 min and the reaction mixture was maintained at −20 °C (in a freezer) for 10 d. After that time, the cold reaction mixture was poured into precooled (−20 °C) acetone (500 ml) containing water (10.5 ml) and the mixture was stirred at room temperature for 3 h. After filtration, the filtrate was concentrated under a pressure of 100 mmHg, and distillation of the residue provided **5** (7.6 g, 64%) as a colorless oil, bp 72—73 °C (18 mmHg), $[\alpha]_D^{20}$ +57.3° (c=0.96, $CHCl_3$) [lit.[6a)] bp 78 °C (18 mmHg), $[\alpha]_D^{20}$ +46.7° (c=1.38, $CHCl_3$)]. ^{1}H-NMR ($CDCl_3$) δ: 2.14 (1H, d, J=2.7 Hz, OH), 2.75 (1H, dd, J=3.9, 5.1 Hz, 1-H), 2.80 (1H, dd, J=2.9, 5.1 Hz, 1-H), 3.09 (1H, m, 2-H), 4.32—4.39 (1H, m, 3-H), 5.26 (1H, dt, J=1.4, 10.2 Hz, 5-H), 5.39 (1H, dt, J=1.4, 17.4 Hz, 5-H), 5.84 (1H, ddd, J=6.4, 10.2, 17.4 Hz, 4-H).

The diastereomer excess (de) of **5** was determined by 300 MHz ^{1}H-NMR ($CDCl_3$) analysis. Nonstereoselective peroxy-acid epoxidation of **4** was performed by the method of Holland and Stoddart[10)] and gave an authentic sample of the epoxide. In the NMR spectrum of **5**, the protons at position 3 appeared as two multiplet signals due to *threo–erythro* configuration at 4.32—4.39 and 3.98—4.07 (intensity ratio = 1217 : 13). The diastereomer excess was calculated, based on the relative intensity of those two peaks, as 98% de.

The enantiomer excess (ee) was determined by 300 MHz ^{1}H-NMR ($CDCl_3$) analysis of the corresponding (S)-(−)-α-methoxy-α-trifluoromethylphenylacetic acid ester (MTPA ester).[11)] The authentic (S)-MTPA ester was prepared from the authentic *erythro*-epoxide. In the NMR spectrum of the (S)-MTPA ester of **5**, the protons at position 1 (nonequivalent methylene protons) appeared as two double doublet signals due to the two diastereomers at 2.73 (J=2.4, 4.8 Hz) and 2.62 (J=2.6, 5.0 Hz) (intensity ratio = 176.5 : 3.1). The enantiomer excess was calculated, based on the relative intensity of those two peaks, as 97% ee.

(2*R*,3*S*)-3-Benzyloxy-1,2-epoxy-4-pentene (6) Sodium hydride (2.1 g, 52.5 mmol, 60% in oil) was added to a solution of **5** (5.0 g, 50.0 mmol), benzyl bromide (9.8 g, 57.5 mmol) and tetrabutylammonium iodide (1.85 g, 5.0 mmol) in dry THF at −20 °C under argon. The mixture was stirred at 0 °C for 2 h and at room temperature for 2 h, then the reaction was quenched by the addition of saturated aqueous NH_4Cl. This solution was extracted with ethyl acetate (AcOEt) and the organic layer was washed with brine. Drying followed by evaporation and purification by silica gel column chromatography (AcOEt: hexane = 1 : 20) afforded **6** (9.1 g, 96%) as a a colorless oil, $[\alpha]_D^{20}$ +35.3° (c=0.93, $CHCl_3$) [lit.[6e)] $[\alpha]_D^{20}$ +32.5° (c=0.96, $CHCl_3$)]. ^{1}H-NMR ($CDCl_3$) δ: 2.69 (1H, dd, J=2.7, 5.1 Hz, 1-H), 2.79 (1H, dd, J=4.1, 5.1 Hz, 1-H), 3.09 (1H, m, 2-H), 3.81 (1H, dd, J=4.2, 7.2 Hz, 3-H), 4.47 and 4.64 (2H, ABq, J=11.6 Hz, benzyl), 5.34 (1H, m, 5-H), 5.38 (1H, s, 5-H), 5.83 (1H, m, 4-H), 7.22—7.40 (5H, m, aromatic).

(2*R*,3*S*)-3-Benzyloxy-1-cyclohexyl-2-mesyloxy-4-pentene (7) Cyclohexylmagnesium chloride [11 ml, 22.0 mmol, 2 M in diethyl ether (Et_2O)] was added to a mixture of cuprous iodide (418 mg, 2.19 mmol) and dry THF (40 ml) at −78 °C under argon. The mixture was stirred for 20 min at −60 °C, then a solution of **6** (2.78 g, 14.6 mmol) in dry THF (10 ml) was added at −60 °C over a period of 15 min. After being stirred at −60 °C for 1.5 h, the reaction mixture was poured into saturated aqueous NH_4Cl. The solution was extracted with AcOEt and the organic layer was washed with brine. Drying followed by evaporation gave a pale yellow oil. The residue was dissolved in CH_2Cl_2 (30 ml), then mesyl chloride (1.66 g, 4.5 mmol) and triethylamine (1.9 g, 18.8 mmol) were added at 0 °C. The reaction mixture was stirred at room temperature for 1 h. After dilution with Et_2O, the mixture was washed with 1 N HCl, saturated aqueous $NaHCO_3$, water and brine. Drying followed by evaporation and purification by silica gel column chromatography (AcOEt : hexane = 1 : 20) afforded **7** (3.2 g, 62%) as a colorless oil, $[\alpha]_D^{20}$ +30.2° (c=0.97, $CHCl_3$). IR (neat): 3450 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.75—1.02 (2H, m, cyclohexyl), 1.03—1.47 (5H, m, cyclohexyl), 1.50—1.75 (5H, m, cyclohexyl and 1-H), 1.85 (1H, m, 1-H), 2.98 (3H, s, mesyl), 3.87 (1H, dd, J=2.4, 7.8 Hz, 3-H), 4.43 and 4.62 (2H, ABq, J=11.9 Hz, benzyl), 4.95 (1H, ddd, J=2.4, 3.9, 9.6 Hz, 2-H), 5.33 and 5.44 (each 1H, m, 5-H), 5.81 (1H, ddd, J=7.8, 10.5, 17.4 Hz, 4-H), 7.22—7.40 (5H, m, aromatic). FAB-MS m/z: $[M+H]^+$ Calcd for $C_{19}H_{29}O_4S$: 353.1787. Found: 353.1754.

(2*S*,3*R*,4*S*)-4-Azido-3-*O*-benzyl-5-cyclohexyl-1,2,3-pentanetriol (8) A mixture of **7** (300 mg, 0.85 mmol) and sodium azide (168 mg, 2.56 mmol) in *N*,*N*-dimethylformamide (5 ml) was stirred at 120 °C for 2 h, and after it had cooled to room temperature, water was added. The solution was extracted with Et_2O and the organic layer was washed with water and brine. Drying followed by evaporation gave a yellow oil. This residue was dissolved in acetone–water (4 ml—0.6 ml), then *N*-methylmorpholine *N*-oxide (200 mg, 70 mmol) and osmium tetroxide (11 mg, 0.043 mmol) were added. The mixture was stirred overnight and saturated aqueous $NaHSO_3$ was added. The solution was extracted with AcOEt and the organic layer was washed with brine. Drying followed by evaporation and purification by silica gel column chromatography (AcOEt : hexane = 1 : 2) afforded **8** (250 mg, 88%) as a colorless oil, $[\alpha]_D^{20}$ −41.2° (c=1.0, $CHCl_3$). IR (KBr): 3424, 2110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.80—1.80 (13H, m, cyclohexyl and 5-H), 1.90 (1H, t, J=5.6 Hz, 1-OH), 2.44 (1H, d, J=5.9 Hz, 2-OH), 3.46—3.90 (5H, m, 1-H, 2-H, 3-H and 4-H), 4.66 and 4.71 (2H, ABq, J=11.6 Hz, benzyl), 7.25—7.42 (5H, m, aromatic). FAB-MS m/z: $[M+K]^+$ Calcd for $C_{18}H_{27}N_3O_3K$: 372.1689. Found: 372.1690.

The optical purity of **8** was determined by 300 MHz ^{1}H-NMR ($CDCl_3$) analysis. An authentic sample was prepared by alkaline hydrolysis (2 N KOH : THF = 1 : 1) of the authentic epoxide (see experimental section, compound **9**). In the NMR spectrum of **8**, the hydroxyl protons at position 2 appeared as two doublet signals due to the two diastereomers at 2.44 (J=5.9 Hz) and 2.48 (J=6.4 Hz) (intensity ratio = 673 : 58). The optical purity was calculated, based on the relative intensity of those two peaks, as 84% de.

(2*S*,3*R*,4*S*)-4-Azido-3-benzyloxy-5-cyclohexyl-1,2-epoxypentane (9) Tosyl chloride (85 mg, 0.45 mmol) was added to a solution of **8** (99 mg, 0.30 mmol) in pyridine (1.5 ml) at 0 °C and the mixture was stirred at room temperature overnight. The reaction mixture was poured into ice-water, then the solution was extracted with AcOEt. The organic layer was washed with 1 N HCl, saturated aqueous $NaHCO_3$, water and brine. Drying followed by evaporation gave a pale yellow oil. This residue was dissolved in methanol (2 ml) and potassium carbonate (83 mg, 0.59 mmol) was added at 0 °C. The mixture was stirred at room temperature for 1 h and acetic acid (35 μl) was added. After dilution with AcOEt, the organic layer was washed with water and brine. Drying followed by evaporation and purification by silica gel column chromatography (AcOEt : hexane = 1 : 12) afforded **9** (68 mg, 73%) as a colorless oil, $[\alpha]_D^{20}$ −25.7° (c=1.06, $CHCl_3$). IR (KBr): 3450, 2110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.78—1.05 (2H, m, cyclohexyl), 1.05—1.80 (11H, m, cyclohexyl and 5-H), 2.71 (1H, dd, J=2.6, 5.3 Hz, 1-H), 2.85 (1H, dd, J=3.8, 5.3 Hz, 1-H), 3.09 (1H, m, 2-H), 3.17 (1H, dd, J=3.8, 6.2 Hz, 3-H), 3.45 (1H, m, 4-H), 4.55 and 4.73 (2H, ABq, J=11.9 Hz, benzyl), 7.25—7.42 (5H, m, aromatic). FAB-MS m/z: $[M+K]^+$ Calcd for $C_{18}H_{25}N_3O_2K$: 354.1584. Found: 354.1585.

The optical purity of **9** was determined by 300 MHz ^{1}H-NMR ($CDCl_3$) analysis. Nonstereoselective epoxidation of (2S,3R)-2-azido-3-benzyloxy-1-cyclohexyl-4-pentene was performed by treatment with *m*-chloroperbenzoic acid in CH_2Cl_2 and gave an authentic sample of the epoxide. In the NMR spectrum of **9**, the protons at position 1 (non-equivalent methylene protons) appeared as two double doublet signals due to the two diastereomers at 2.54 (J=2.9, 5.0 Hz) and 2.71 (J=2.2, 5.3 Hz) (intensity ratio = 14.3 : 159.5). The optical purity was calculated, based on the relative intensity of those two peaks, as 84% de.

(2*S*,3*R*,4*S*)-4-Azido-3-*O*-benzyl-5-cyclohexyl-1-morpholino-2,3-pentanediol (10) A mixture of **9** (34 mg, 0.11 mmol) and morpholine (100 μl) in EtOH (1 ml) was refluxed for 2 h. Evaporation followed by purification by silica gel column chromatography (AcOEt : hexane = 1 : 2) gave **10** (42.3 mg, 98%) as a colorless oil. $[\alpha]_D^{20}$ −43.3° (c=1.13, $CHCl_3$). IR (KBr): 3450, 2110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.78—1.05 (2H, m, cyclohexyl), 1.05—1.80 (11H, m, cyclohexyl and 5-H), 2.30—2.45 and 2.52—2.72 (each 3H, m, 1-H and *N*-methylene), 3.41 (1H, dd, J=2.9, 6.6 Hz, 4-H), 3.52 (1H, m, 4-H), 3.60—3.78 (4H, m, *O*-methylene), 3.87 (1H, m, 2-H), 4.65 and 4.70 (2H, ABq, J=11.6 Hz), 7.20—7.40 (5H, m, aromatic). FAB-MS m/z: $[M+H]^+$ Calcd for $C_{22}H_{35}N_4O_3$: 403.2709. Found: 403.2734.

(2*S*,3*R*,4*S*)-4-*tert*-Butoxycarbonylamino-5-cyclohexyl-1-morpholino-

2,3-pentanediol (Boc-ACMP), (11) A suspension of 10% Pd–C (20 mg) in AcOEt (0.5 ml) was stirred under a hydrogen atmosphere for 30 min. To this suspension was added a mixture of **10** (137 mg, 0.34 mmol) and di-*tert*-butyl dicarbonate (89 mg, 0.41 mmol) in AcOEt (1.5 ml), and the resulting mixture was stirred under hydrogen at room temperature overnight. Filtration and removal of the solvent gave a white solid. Recrystallization from AcOEt–hexane afforded **11** (100.4 mg, 76%) as colorless needles, mp 143.5—145.0 °C. $[\alpha]_D^{20}$ −15.8° (c = 1.07, $CHCl_3$). IR (KBr): 3442, 1680 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 0.76—1.07 (2H, m, cyclohexyl), 1.08—1.87 (11H, m, 5-H and cyclohexyl), 1.45 (9H, s, *tert*-butyl), 2.55 (2H, m, *N*-methylene), 2.57—2.87 (4H, m, *N*-methylene), 3.34—3.55 (2H, m, 2-H and 3-H), 3.55—3.82 (4H, m, *O*-methylene), 3.97 (1H, m, 4-H), 4.66 (2H, br d, J = 9.9 Hz, NH and OH). ^{13}C-NMR ($CDCl_3$) δ: 26.1, 26.6, 26.5, 32.8, and 33.6 (each t, cyclohexyl), 34.2 (d, cyclohexyl), 28.3 (q × 3, methyl × 3), 38.9 (t, 5-C), 48.1 (d, 2-C), 54.3 (t × 2, *N*-methylene × 2), 64.3 (d and t, 1-C and 2-C or 3-C), 66.7 (t × 2, *O*-methylene × 2), 79.8 (d, 2-C or 3-C), 80.0 (s, $-\underline{C}-CO-$), 157.6 (s, –CO–). MS m/z: $[M+H]^+$ Calcd for $C_{20}H_{39}N_2O_5$: 387.2859. Found: 387.2835.

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