Pergamon

*Tetrahedron*, Vol. 52, No. 6, pp. 2187-2192, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01049-1

# A Facile Formal Synthesis of D-ribo-$C_{18}$-Phytosphingosine

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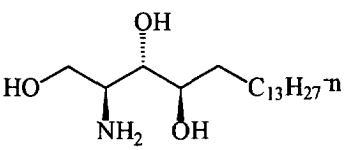
**Abstract:** A facile synthesis of D-ribo-$C_{18}$-Phytosphingosine from divinylcarbinol *via* Sharpless asymmetric epoxidation and Sharpless asymmetric dihydroxylation was described.

$C_{18}$-Phytosphingosine ((*2S,3S,4R*)-2-amino-octadecane-1,3,4-triol) and its related $C_{20}$-homologue, are widely distributed as amides of α-hydroxyl long chain acids in plant sphingolipids.[1] It is also reported that phytosphingosine is present in human brain and kidney lipids.[2] Large amounts of the corresponding $C_{20}$-homologue of Sphingosine and Phytosphingosine were detected in the gangliosides of the brain. Whereas $C_{18}$-Phytosphingosine is encountered in addition to Sphingosine especially in the skin.[3]



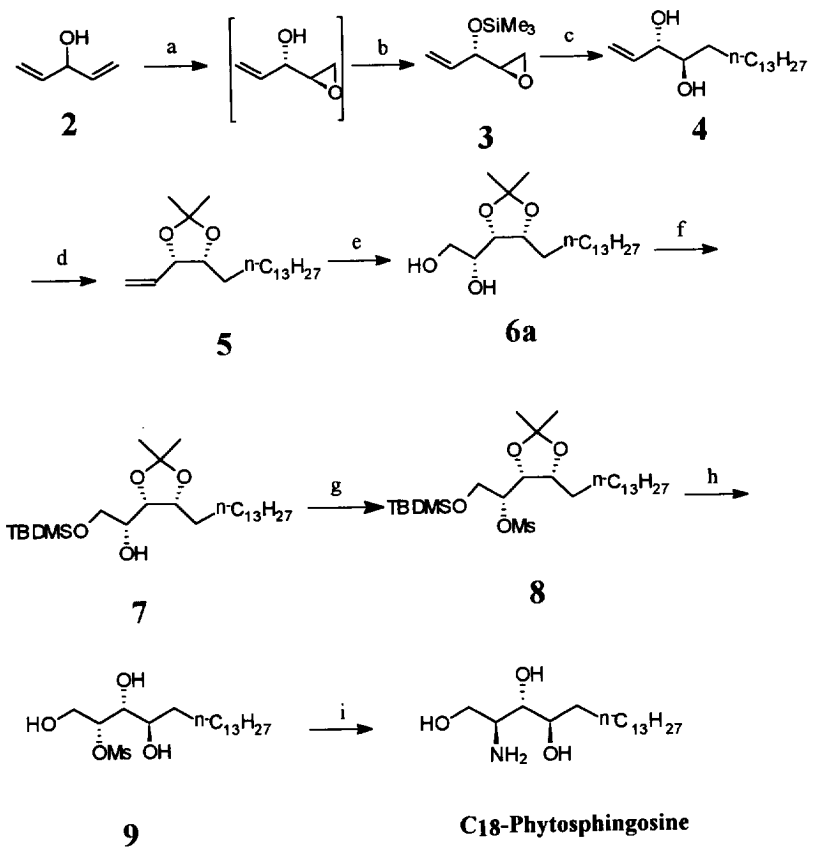

**Phytosphingosine**

Owing to the biological importance of the Phytosphingosine, several syntheses of the racemic[4] and the optically active material[5] have been described. But the search for new and improved procedures remains unabated. Here we reported a facile synthesis of $C_{18}$-Phytosphingosine with the Sharpless asymmetric epoxidation (AE)[6] and Sharpless asymmetric dihydroxylation(AD).[7]

It is reported that the chiral 1,2-epoxy-4-penten-3-ol generated by Sharpless asymmetric epoxidation of divinylcarbinol(**2**)[8] is a versatile building blocks for the synthesis of some natural products.[9] The Sharpless asymmetric dihydroxylation is also a useful strategy toward the synthesis of some carbohydrates and polyhydroxylated natural compounds.[10] Here we report the synthesis of $C_{18}$-Phytosphingosine using these two methods . It is outlined in Scheme 1.

The trimethylsilyloxy oxirane (**3**) was readily obtained in 65% yield from divinylcarbinol (**2**) using Sharpless asymmetric epoxidation with high de (98%) and ee (97%). Regioselective ring opening of **3** with n-tridecyl magnesium bromide in the presence of copper (I) iodide followed by removal of silyl group with 5% aq. HCl gave diol (**4**) in 85% yield. Protection of the diol in **4** with dimethoxy propane easily provided the isopropylidene derivative (**5**) in 98% yield. Dihydroxylation of **5** with Sharpless condition gave a

diastereoisomer (**6a** and **6b**). The ratio of 6a/6b varies depending on the reaction condition. The results were outlined in Scheme 2. In the absence of the chiral ligand, the ***thero*** product **6b** was predominant due to the substrate control, the ratio of 6a/6b was 1/10. This is consistent with Kishi's empirical rule.[11] When the DHQ-CLB (Aldrich, No: 33649-1) was used as the chiral ligand, equal amount of **6a** and **6b** was obtained. The desired product **6a** became favoured when the $(DHQ)_2PHAL$ (Aldrich, No: 39272-3) was used as the chiral



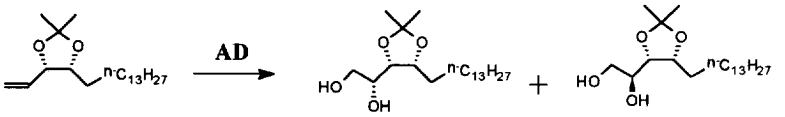

**Scheme 1**

Reaction Conditions:
a: L-(+)-DIPT, TBHP, $Ti(OPr^i)_4$, 4 Å molecular sieves, $CH_2Cl_2$, -20°C, 10days; b: $Me_3SiCl$, DMAP, $Et_3N$, $CH_2Cl_2$, 0°C, 65% from 1; c: $n\text{-}C_{13}H_{27}MgBr$, CuI(10%), THF, -10°C, 85%; d: $(CH_3)_2C(OMe)_2$, PTS acid, $CH_2Cl_2$, r.t., 98%; e: $OsO_4$(cat), $K_3Fe(CN)_6$, $K_2CO_3$, $(DHQ)_2PHAL$, t-BuOH / $H_2O$ = 1 / 1, r.t., 92% (d.r. = 4 : 1); f: TBDMS-Cl, Imidazole, DMF, 0°C, 91%; g: MsCl, pyridine, $CH_2Cl_2$, r.t., 90%; h: PTS-acid/MeOH, 10% aq. HCl , 85%; i: Ref 5e

ligand, the ratio of 6a/6b was 4/1. Protection of the primary alcohol **6a** with *tert*-butyldimethylsilyl chloride gave 7 (91%). Then mesylation of alcohol in 7 provided **8** (90%). Removal of the ketal group and silyl group with *p*-toluenesulfonic acid and 10% aq. HCl gave the triol (**9**) in 85% yield. According to the method of

Schmidt, **9** was treated with sodium azide followed by reduction with lithiumaluminium hydride gave the desired D-ribo-$C_{18}$-Phytosphingosine.[5c]

Thus, we furnished the formal synthesis of D-ribo-$C_{18}$-Phytosphingosine with 7 steps in 27.7% overall yield from **2** to **9**.




**5** **6a** **6b**

| | | |
|---|---|---|
| **A:** | **NO LIGAND** | **6a/6b = 1/10** |
| **B:** | **DHQ-CLB** | **6a/6b = 1/1** |
| **C:** | **(DHQ)$_2$PHAL** | **6a/6b = 4/1** |

## Scheme 2

## Experimental:

Melting points were measured on a Büchi 535 spectrometer and were uncorrected. Infrared spectra were recorded on a Shimadzu IR-440 spectrometer and only the strongest/structurally most important peaks were listed in $cm^{-1}$. $^1H$ NMR spectra were obtained at Bruker AM 300(300 MHz) spectrometer using TMS as internal standard. Routine mass spectra were run on a Finnigan 4021 and HP 5989A apparatus. HRMS were recorded on Finnigan MAT spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at the sodium D line at 25°C. Flash column chromatography were carried out using silica gel (200-300 mesh, made in Shanghai, China).

**(*2R,3S*)-1,2-Epoxy-3-trimethylsilyloxy-4-pentene(3):** To a mixture of 6g of 4 Å molecular sieves and 150 ml of dried $CH_2Cl_2$, were added subsequently 2.0 ml of L-(+)-DIPT(9.5 mmol), 15 ml of TBHP(7.4 M in $CH_2Cl_2$) and 3.0 ml of $Ti(OPr^i)_4$ (10.0mmol) at -20°C under positive $N_2$ pressure. After stirring for 0.5 hr, 6 ml of divinylcarbinol (62.0 mmol) were added *via* syringe. The mixture was kept in refrigerator at -20°C for 10 days. 1.2 g of citric acid (6.2 mmol) and 120 ml of 10% $H_2O$ in acetone were added. The mixture was stirred at r.t. for 1 hr then was filtered through a pad of celite. Removal of solvent gave a yellow oil, which was then dissolved in 250 ml of $CH_2Cl_2$. 25 ml of triethylamine (79.4 mmol), 1.5 g of DMAP (12.3 mmol) and 19 ml of trimethylsilyl chloride (90.0 mmol) were then added to the mixture at 0°C. The resultant mixture was stored in a refrigerator at -10°C for 24 hr, then was filtered through a pad of celite, washed with sat. aq. NaCl and dried over anhy. $Na_2SO_4$. Removal of solvent and purification by flash column chromatography gave 10.3 g of pure **3** as a colorless oil in 65% yield. $[\alpha]_D$ -7.8° (c, 1.1, $CHCl_3$). $\nu_{max}$: 2900; 1640; 1260 $cm^{-1}$. $\delta_H(CDCl_3)$: 5.71 (1H,

m, 4-H); 5.10 (1H, dd, J=9.6, 1.5 Hz, 5-H); 5.02 (1H, d, J=11.2 Hz, 5'-H); 3.90 (1H, m, 3-H); 2.65 (1H, m, 2-H); 2.40 (2H, m, 1-H) ppm. m/z (%): 172 ($M^+$, 1.50); 171 ($M^+$-1, 0.2); 73 ($SiMe_3$, base).

**(*3S,4R*)-3,4-Dihydroxy-1-octadecene (4):** To a solution of 3.195 g of **3** (18.6 mmol) in 15 ml of anhydrous THF, was added 353 mg of copper (I) iodide (1.86 mmol). n-Tridecyl magnesium bromide (prepared from 0.53 g of magnesium, 5.2 ml of 1-bromotridecane in 15 ml of THF) was added dropwise at -10°C. The mixture was stirred and gradually warmed to r.t.. After the completion of the reaction monitored by TLC, 25 ml of sat. aq. $NH_4Cl$ was added to quench the reaction. Then 25 ml of 10% aq. HCl was added to remove the silyl group. Removal of THF under reduced pressure gave a mixture, which was extracted with ethyl acetate, washed with sat. aq. NaCl and dried over anhydrous $Na_2SO_4$. Removal of solvent and purification by flash column chromatography (petroleum ether : ethyl acetate = 4 : 1) gave 4.48 g of pure **4** as a white solid. m.p.: 48.2-48.7°C. $[\alpha]_D$ -12.6° (c, 0.25, $CHCl_3$). $\nu_{max}$: 3250 (br, -OH); 2900; 2820; 1460 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 5.92 (1H, m, 2-H); 5.38 (1H, d, J=17.2 Hz, 1-H); 5.30 (1H, d, J=10.3 Hz, 1'-H); 4.13 (1H, m, 3-H); 3.68 (1H, m, 4-H); 2.08 (2H, br, 2 x OH); 1.15-1.65 (26H, m, 13 x $CH_2$); 0.89 (3H, t, J=6.47 Hz, $CH_3$) ppm. FABMS: 284 ($M^+$). m/z (%): 267 (M+1-$H_2O$, 3.7%). $C_{18}H_{36}O_2$: Calcd: C: 76.05; H: 12.68. Found: C: 75.80; H: 12.78.

**(*3S,4R*)- 3,4-*O*-isopropylidene-1-octadecene (5):** To a solution of 2.84 g of **4** (10.0 mmol) in 30 ml of dried $CH_2Cl_2$, was added 190 mg of *p*-toluenesulfonic acid (1.0 mmol) followed by addition of 2.5 ml of 2,2-dimethoxy propane (15.0 mmol). The reaction mixture was stirred at ambient temperature until the completion of the reaction monitored by TLC (about 30 min). 2g of $NaHCO_3$ (23.8 mmol) in 10 ml of water was poured into the flask, the mixture was extracted with $CH_2Cl_2$ 3 times. The combined organic layer was dried over anhydrous $Na_2SO_4$, then subjected to flash column chromatography (petroleum ether : ethyl acetate = 50 : 1) to produce 3.17 g of **5** as a pale viscous oil in 98% yield. $[\alpha]_D$ +6.5° (c, 0.37, $CHCl_3$). $\nu_{max}$: 2900; 2820; 1460; 1240 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 5.71 (1H, m, 2-H); 5.28 (1H, d, J=17.1 Hz, 1-H); 5.22 (1H, d, J=10.4 Hz, 1'-H); 4.48 (1H, dd, $J_{23}$=$J_{34}$=6.74 Hz, 3-H); 4.14 (1H, m, 4-H); 1.48 (3H, s, $CH_3$); 1.37 (3H, s, $CH_3$); 1.18-1.48 (26H, m, 13 x $CH_2$); 0.88 (3H, t, J=6.1 Hz, $CH_3$) ppm. m/z (%): 309 (M-$CH_3$, 34); 225 (M-$C_7H_{15}$ , 36); 99 ($C_7H_{15}$ , base). HRMS: Calcd for $C_{20}H_{37}O_2$ (M-$CH_3$) 309.2793; Found: 309.2758.

**(*2R,3R,4R*)-1,2-Dihydroxy-3,4-*O*-isopropylidene-octadecane (6):** 648 mg of **5** (2.0 mmol) was dissolved in mixture of 20 ml of t-BuOH and 20 ml of water. 1.98 g of $K_3Fe(CN)_6$ (6.0 mmol) and 833 mg of $K_2CO_3$ (6.0 mmol) and 390 mg of $(DHQ)_2PHAL$ (0.5 mmol) were added, followed by dropwise addition of 1.0 ml of $OsO_4$ solution (0.5 g $OsO_4$ in 40 ml of t-BuOH). The resultant mixture was stirred at r.t. for 24 hr. 2.7 g of sodium sulfite (21.4 mmol) was added to quench the reaction. The reaction mixture was concentrated to remove *t*-BuOH, then extracted with ethyl acetate 4 times. Finally, removal of solvent gave a residue which was chromatographed on silica gel, eluting with petroleum ether and ethyl acetate (PE : EtOAc = 4 : 1) to produce 527 mg of **6a** and 132 mg of **6b**. Spectra data of **6a**: m.p.: 45.5-46.5°C. $[\alpha]_D$ -14.2° (c, 0.40, $CHCl_3$). $\nu_{max}$: 3350 (br, -OH); 2900; 2820; 1465; 1380 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 4.04 (1H, m, 3-H); 3.71 (2H, d, J=4.4 Hz, 1-H); 3.65 (2H, m, 2-H and 4-H); 2.22 (2H, br, 2 x OH); 1.52 (2H, m, 5-H); 1.43 (6H, m, 2 x $CH_3$); 1.15-1.26 (24H, m, 12 x $CH_2$); 0.88 (3H, t, J=6.1 Hz, $CH_3$) ppm. m/z (%): 359 (M+1, 1.47); 343 (M-$CH_3$, 99.5). HRMS: Calcd for $C_{20}H_{39}O_4$ (M-$CH_3$) 343.2849; Found: 343.2822. Spectra data of **6b**: m.p.: 52.5°C. $[\alpha]_D$ -8.8° (c, 0.84, $CHCl_3$). $\nu_{max}$: 3350; 2900; 2810; 1460; 1380 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 3.96 (2H, m, 3-H and 4-H); 3.74 (3H, m,

1-H and 2-H); 2.07 (2H, br, 2 x OH); 1.39 (3H, s, $CH_3$); 1.37 (3H, s, $CH_3$); 1.18-1.28 (26H, m, 13 x $CH_2$); 0.88 (3H, t, J=6.2 Hz, $CH_3$) ppm. m/z (%): 343 (M-$CH_3$, 51.0).

**(*2R,3R,4R*)-1-*tert*-Butyldimethylsilyloxy-2-hydroxy-3,4-*O*-isopropylidene-octadecane (7):** To a solution of 358 mg of **6a** (1.0 mmol) in 6 ml of DMF, was added 115 mg of imidazole (1.69 mmol). 226 mg of tert-butyldimethylsilyl chloride (1.5 mmol) was added at 0°C and the resultant mixture was stirred at 0°C for 2 hr. 3 ml of water was added to quench the reaction. The reaction mixture was then extracted with $Et_2O$ (4 times). The ethereal layer were combined and concentrated, then was subjected to the flash column chromatography (petroleum ether : ethyl acetate = 40 : 1) to afford 430 mg of **7** as a pale viscous oil in 91% yield. $[\alpha]_D$ -22.2° (c, 0.1, $CHCl_3$). $\nu_{max}$: 3350; 2900; 2810; 1460; 1360 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 4.13 (1H, m, 3-H); 3.98 (1H, dd, J=9.2 and 5.8 Hz, 4-H); 3.85 (1H, dd, J=10.2 and 2.5 Hz, 2-H); 3.62 (2H, m, 1-H); 1.38 (3H, s, $CH_3$); 1.23 (3H, s, $CH_3$); 1.20-1.48 (26H, m, 13 x $CH_2$); 0.92 (9H, s, 3 x $CH_3$); 0.86 (3H, t, J=6.7 Hz, $CH_3$); 0.0(6H, s, 2 x $CH_3$) ppm. m/z (%): 471 (M-1, 0.2); 457 (M-CH3, 15.2); 297 (M-TBDMS, 47.4). HRMS: Calcd for $C_{27}H_{55}O_4$ (M-1) 471.3870; Found: 471.3835. Calcd for $C_{26}H_{53}O_4$ (M-$CH_3$) 457.3713; Found: 457.3695.

**(*2R,3R,4R*)-1-*tert*-Butyldimethylsilyloxy-2-mesyloxy-3,4-*O*-isopropylidene-octadecane (8):** 236 mg of **7** (0.5 mmol) was dissolved in 2.5 ml of $CH_2Cl_2$. 1.5 ml of pyridine and 0.1 ml of methanesulfonic chloride (1.3 mmol) were then added dropwise at room temperature. The resultant mixture was stirred at r.t. for 4 hr, then was diluted with 100 ml of $CH_2Cl_2$ and washed with sat. aq. $CuSO_4$ to remove the pyridine. Finally, removal of the solvent gave a residue which was subjected to flash column chromatography (petroleum ether : ethyl acetate = 40 : 1) to generate 248 mg of **8** as a pale viscous oil in 90% yield. $[\alpha]_D$ -14.0° (c, 0.14, $CHCl_3$). $\nu_{max}$: 2920; 2850; 1460; 1360 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 4.61 (1H, dt, J=5.9 and 4.4 Hz, 2-H); 4.01 (1H, dt, J=8.0 and 3.3 Hz, 4-H); 3.87 (2H, d, J=5.9 Hz, 1-H); 3.81 (1H, m, 3-H); 3.09 (3H, s, $CH_3$); 1.56 (2H, m, 5-H); 1.39 (6H, s, 2 x $CH_3$); 1.18-1.29 (24H, m , 12 x $CH_2$); 0.89 (9H, s, 3 x $CH_3$); 0.86 (3H, t, J=6.1 Hz, $CH_3$); 0.09 (6H, s, 2 x $CH_3$) ppm. m/z (%): 535 (M-$CH_3$, 14.6). HRMS: Calcd for $C_{27}H_{55}SiSO_6$ (M-$CH_3$) 535.3489; Found: 535.3480.

**(*2R,3R,4R*)-2-*O*-Methanesufonyl-1,2,3,4-octadecanetetrol (9):** To a solution of **8** (0.364 mmol) in 3 ml of methanol, 104 mg of *p*-toluenesulfonic acid (0.55 mmol) was added. The resultant mixture was stirred at r.t. for 1.5 hr. Then 5 ml of 20% aq. HCl was added to the mixture and the resultant mixture was stirred at r.t. for 2hr. Removal of methanol under reduced pressure gave a residue which was extracted with ethyl acetate 4 times. The combined organic layer was concentrated and then purified by flash column chromatography (CH2Cl2 : MeOH = 18 : 1) to produce 123 mg of **9** as white solid in 85% yield. The spectra data is compatible with the literature.[5c] m.p.: 125-126°C. $[\alpha]_D$ +11.2° (c, 0.5, $CHCl_3$/MeOH = 1/1). (Lit: m.p.: 126°C. $[\alpha]_D$ +10° (c, 1.0, $CHCl_3$/MeOH = 1/1). $\nu_{max}$: 3340; 2920; 1360 $cm^{-1}$. $^1H$ NMR ($d_6$-DMSO): 4.45, 4.85, 5.00 (br, 3 x -OH); 4.71 (1H, m, 2-H); 3.56 (1H, m, 1-H); 3.48 (1H, m, 1'-H); 3.31-3.38 (2H, m, 3-H and 4-H); 3.15 (3H, s, $CH_3$); 1.44 (2H, m, 5-H); 1.15-1.36 (24H, m, 12 x $CH_2$); 0.88 (3H, t, J=6.2 Hz, $CH_3$) ppm. m/z (%): 379 (M+1-$H_2O$, 15.1); 301 (M-OMs, 45.3).

## Acknowledgment:

We are grateful to the National Natural Science Foundation of China for financial support.

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(*Received in UK* 8 *September* 1995; *revised* 28 *November* 1995; *accepted* 30 *November* 1995)