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# Stereoselective synthesis of (–)-tetrahydropyrenophorol

VYASABHATTAR RAMANUJAN, SHAIK SADIKHA
and CHEBOLU NAGA SESHA SAI PAVAN KUMAR*

*Division of Chemistry, Department of Sciences and Humanities, Vignan's Foundation for Science, Technology & Research (VFSTR) University, Vadlamudi, Guntur 522 213, Andhra Pradesh, India*

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*Abstract*: Tetrahydropyrenophorol, an interesting macrodiolide, was isolated from the plant *Fagonia cretica*. The total synthesis of (–)-1-tetrahydropyrenophorol was achieved in an elegant and linear manner from readily an accessible racemic epoxide. The archetypal reactions include regioselective opening of the epoxide, Sharpless asymmetric dihydroxylation, and Mitsunobu cyclodimerization to construct the requisite 16-membered bis-lactone. The synthetic approach demonstrated here is very simple and could be used for the syntheses of related compounds in an economic and highly stereoselective way.

*Keywords*: macrodiolide; sharpless asymmetric dihydroxylation; Mitsunobu reaction; stereoselectivity.

## INTRODUCTION

The synthesis of natural products is one of the most enthralling and exigent areas of research in chemistry.[1] Macrodiolides are well represented in nature as both homo and heterodimers and proffer a wide variety of skeletons, ring sizes, and functional groups. Macrocyclic dilactones also have a range of biological activities, *e.g.*, antifungal,[2–4] antihelmintic,[5–7] phytotoxic[8–10] and antileukemic[11] activity. (–)-Tetrahydropyrenophorol (Fig. 1), a new macrodiolide, isolated from the plant *Fagonia cretica* exhibits good herbicidal and moderate fungicidal activities. The structure of the (–)-tetrahydropyrenophorol (**1**) is a 16-membered bis--lactone having four asymmetric centres. It was explicated by spectroscopic methods and X-ray analysis.[12] Originally, (–)-tetrahydropyrenophorol was synthesized by Oh and co-workers[13] starting from *α*-D-glucopyranoside using the Yamaguchi protocol as a key step. Later Pratapreddy *et al.*[14] accomplished the concise synthesis of tetrahydropyrenophorol from chiral epoxide. Recently, Mahesh *et al.*[15] achieved the synthesis of tetrahydropyrenophorol from *p*-meth-

* Corresponding author. E-mail: pavaniict@gmail.com
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oxybenzyloxy-epoxide while Trost and Quintard reported the synthesis of its (+)--congener.[16] In continuance of efforts on the synthesis of natural products, especially macrocyclic systems,[17,18] a fastidious and stereoselective total synthesis of (–)-tetrahydropyrenophorol is described. The Sharpless asymmetric dihydroxylation and Mitsunobu cyclodimerization were adopted as crucial steps, as described in earlier methods.[14,15] Sharpless dihydroxylation is very simple and useful for the construction of new stereogenic centres and in the present case, the yield was very good. For the cyclodimerization, the standard Mitsunobu reaction was used in the penultimate step, but, overall, the presented synthetic strategy is diverse and elegant. The present approach is simple and efficient compared to other methods and could be useful for the syntheses of related compounds.

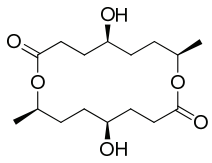



Fig. 1. Structure of (–)-tetrahydropyrenophorol (**1**).

## EXPERIMENTAL

### *General methods*

All chemicals and reagents, obtained from Sigma–Aldrich, Merck or Lancaster, were used without further purification. All solvents were distilled and dried prior to use. Reactions were monitored using Thin Layer Chromatography, performed on silica gel glass plates containing 60 F-254, and visualization was attained by UV light and/or iodine indicator. $^{1}$H- and $^{13}$C-NMR spectra were recorded at 300 and 75 MHz, respectively, using $CDCl_3$ as the solvent. Chemical shifts ($\delta$) are reported in ppm downfield from the internal TMS standard. *J* are coupling constant between the multiplet (interaction between a pair of protons). ESI spectra were recorded on a Micromass, Quattro LC using ESI+ software and ESI mode positive ion trap detector. Melting points were determined using an electrothermal melting point apparatus. The FT-IR spectra were taken on a IR spectrophotometer using NaCl optics. Optical rotation values were recorded on a digital polarimeter at 25 °C.

Spectral and analytical data of the synthesized compounds are given in Supplementary material to this paper.

### *Experimental procedure for the synthesized compounds*

*(*R*)-5-(4-Methoxybenzyloxy)-1-(2-vinyl-1,3-dithian-2-yl)pentan-2-ol (**3**)*. To a stirred solution of 2-vinyl dithiane (3.3 g, 22.7 mmol) in dry THF (30 mL) cooled at –78 °C, a 1.6 M solution of *n*-BuLi in hexane (22.9 mL, 37.82 mmol) was added dropwise. The reaction mixture was stirred at –20 °C for 1 h. After cooling to –78 °C, a solution of epoxide **5** (4.2 g, 18.91 mmol) in THF (10 mL) was added dropwise, and the mixture was kept at –30 °C for 2 h. The reaction was quenched with water (50 mL), and the mixture was extracted with $Et_2O$ (2×100 mL). The combined extracts were washed with brine (100 mL), dried ($Na_2SO_4$), and concentrated. The residual oil was purified by column chromatography on silica gel chromatography (60–120 silica gel, 10 % EtOAc in petroleum ether) to give **3** (5.6 g, 81 %) as a colourless oil.

*(*R*)*-tert-*Butyl(5-(4-methoxybenzyloxy)-1-(2-vinyl-1,3-dithian-2-yl)pentan-2-yloxy)di-phenylsilane (**6**).* To a stirred solution of alcohol **3** (5.1 g, 13.85 mmol) and imidazole (1.41 g, 20.77 mmol) in dry $CH_2Cl_2$ (30 mL) was added TBDPSCl (4.57g, 16.63 mmol) at 0 °C under a nitrogen atmosphere and stirred at room temperature for 4 h. The reaction mixture was quenched with aq. $NH_4Cl$ solution (10 mL) and extracted with $CH_2Cl_2$ (2×50 mL). The combined extracts were washed with water (30 mL), brine (30 mL), dried ($Na_2SO_4$) and concentrated. The residue was purified by column chromatography (60–120 Silica gel, 5 % EtOAc in petroleum ether) to furnish **6** (6.6 g, 79 %) as a colourless liquid.

*(*S*)-1-(2-((*R*)-2-(*tert-*Butyldiphenylsilyloxy)-5-(4-methoxybenzyloxy)pentyl)-1,3-dithian-2-yl)ethane-1,2-diol (**7**).* A mixture of AD-mix-*β* (7.1 g, 9.07 mmol) in 50 mL of *t*-BuOH/$H_2O$ (1:1 volume ratio) was stirred at room temperature for 15 min, and then cooled to 0 °C. To this solution was added silyl ether **6** (5.0 g, 8.25 mmol). The reaction mixture was stirred at 0 °C for 48 h and then quenched with $Na_2SO_3$ (7.5 g) at 0 °C within 0.5 h. EtOAc was added to the reaction mixture, and the aqueous layer was further extracted with twice EtOAc. The combined organic layers were dried over $Na_2SO_4$ and the solvents were evaporated. The crude product was purified by column chromatography on silica gel (hexanes/EtOAc 1:1) to give the corresponding diol **7** (4.33 g, 82 %) as a colourless oil.

The $^1$H-NMR spectrum of the crude dihydroxylated compound **7** was recorded to predict the diastereoselectivity. The spectrum depicted distinctive singlets at $\delta$ values 3.68 and 3.58 ppm with a ratio of ≈9:1 corresponding to the –OC**H**$_3$ group of the PMB protection. Another set of signals could be identified as triplets related to –C**H** of the secondary hydroxyl group at $\delta$ values 3.48 and 3.32 ppm, integration ratio 9:1. From this, the diastereoselectivity of dihydroxylation was assigned as 9:1.

*(*S*)-1-(2-((*R*)-2-(*tert-*Butyldiphenylsilyloxy)-5-(4-methoxybenzyloxy)pentyl)-1,3-dithian-2-yl)ethanol (**8**).* To a stirred solution of diol **7** (4.1 g, 6.40 mmol) in dry dichloromethane (30 mL), triethylamine (1.74 mL, 12.8 mmol) and $Bu_2SnO$ (catalytic amount) were added. After 5 min, *p*-toluene sulfonyl chloride (1.21 g, 6.40 mmol) was added and the mixture stirred at room temperature for 30 min. The reaction was monitored by TLC. After completion of the reaction, the mixture was quenched by adding water (10 mL). The solution was extracted with DCM (3×20 mL) and then the combined organic phase was washed with water, dried ($Na_2SO_4$), and concentrated to give tosylate **7a**.

To a stirred suspension of LAH (0.3 g, 7.68 mmol) in dry THF (5 mL), the above crude tosylate **7a** in dry THF (20 mL) was added dropwise at 0 °C under a nitrogen atmosphere and the mixture stirred for 12 h at room temperature. The reaction mixture was cooled to 0 °C, treated with saturated aq. $Na_2SO_4$ solution, filtered and the filtrate was dried ($Na_2SO_4$) and concentrated. The residue was purified by column chromatography (60–120 Silica gel, 15 % EtOAc in petroleum ether) to give **8** (3.0 g, 77 %) as a colourless syrup.

tert-*Butyl((*R*)-1-(2-((*S*)-1-(*tert-*butyldimethylsilyloxy)ethyl)-1,3-dithian-2-yl)-5-(4-methoxybenzyloxy)pentan-2-yloxy)diphenylsilane (**9**).* A stirred solution of alcohol **8** (2.8 g, 4.48 mmol) and imidazole (0.6 g, 8.96 mmol) in dry $CH_2Cl_2$ (30 mL) was treated with TBSCl (0.80g, 5.38 mmol) at 0 °C under a nitrogen atmosphere and stirred at room temperature for 4 h. The reaction mixture was quenched with aq. $NH_4Cl$ solution (10 mL) and extracted with $CH_2Cl_2$ (2×50 mL). The combined extracts were washed with water (30 mL), brine (30 mL), dried ($Na_2SO_4$) and concentrated. The residue was purified by column chromatography (60–120 silica gel, 5 % EtOAc in petroleum ether) to furnish **9** (2.7 g, 81 %) as a colourless liquid.

*(4*R*,7*S*)-7-(*tert-*Butyldimethylsilyloxy)-4-(*tert-*butyldiphenylsilyloxy)octan-1-ol (**10**).* Commercially available Raney nickel (20.0 g with water, Grade: Raney 2800 nickel from Aldrich)

as a slurry in water was weighed into a 100 mL round-bottomed flask and washed with anhydrous ethanol (10 mL) three times under a nitrogen atmosphere. Compound **9** (2.4 g, 3.25 mmol) in 25 mL ethanol was added *via* a syringe to the slurry mixture before hydrogen gas was bubbled through for 20 min. The mixture was heated to 80 °C and kept at that temperature for 15 h with stirring under a hydrogen atmosphere before it was allowed to attain room temperature. The liquid phase was transferred carefully using a pipette to separate it from residual flammable Raney nickel and washed with ethanol (4×8 mL). The combined liquid was concentrated and purified by column chromatography (Silica gel, 60–120 mesh, 20–25 % EtOAc in petroleum ether) to give acid **10** (1.3 g, 78 %) as a colourless oil.

*(4*S*,7*S*)-7-(*tert-*Butyldimethylsilyloxy)-4-(*tert-*butyldiphenylsilyloxy)octanoic acid (**11**)*. To a stirred solution of **10** (1.2 g, 2.33 mmol) in $CH_2Cl_2$:$H_2O$ (1:1, 1 mL) TEMPO (0.12 g, 0.77 mmol) and BAIB (2.25 g, 6.99 mmol) were added at 0 °C and the mixture stirred for 2 h. The reaction mixture was diluted with water (5 mL) and extracted with $CH_2Cl_2$ (2×20 mL). Organic layers were washed with brine (10 mL), dried ($Na_2SO_4$), evaporated and purified the residue by column chromatography (Silica gel, 60–120 mesh, 20–25 % EtOAc in petroleum ether) to give acid **11** (0.92 g, 75 %) as a colourless gummy oil.

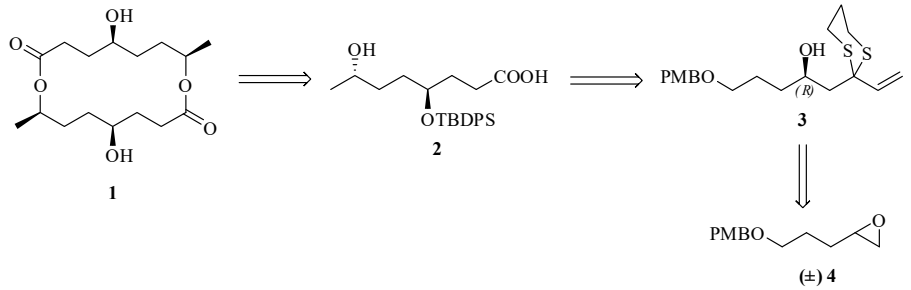
*(4*S*,7*S*)-4-(*tert-*Butyldiphenylsilyloxy)-7-hydroxyoctanoic acid (**2**)*. To a solution of **11** (0.85 g, 1.60 mmol) in ethanol (3 mL), PPTS (0.48 g, 1.92 mmol) was added and the mixture stirred for 3 h at 50 °C. The ethanol was removed and the reaction mixture extracted with ethyl acetate (2×20 mL). The organic layers were washed with water (2×10 mL), brine (10 mL) and dried ($Na_2SO_4$). The solvent was evaporated and the residue purified by column chromatography (60–120 silica gel, 10 % EtOAc in petroleum ether) to furnish **2** (0.60 g, 91 %) as a colourless liquid.

*(5*S*,8*R*,13*S*,16*R*)-5,13-Bis(*tert-*butyldiphenylsilyloxy)-8,16-dimethyl-1,9-dioxacyclo-hexadecane-2,10-dione (**12**)*. To a solution of **2** (0.5 g, 1.2 mmol) and $Ph_3P$ (1.22 g, 4.8 mmol) in toluene:THF (10:1, 550 mL), DEAD (3.0 mL, 18.0 mmol) was added at –25 °C and the mixture stirred under a $N_2$ atmosphere for 10 h. The solvent was evaporated under reduced pressure and the residue purified by column chromatography (60–120 silica gel, 10 % EtOAc in petroleum ether) to afford **12** (0.28 g, 56 %) as a colourless oil.

*(–)-Tetrahydropyrenophorol (**1**)*. To a cooled (0 °C) solution of **12** (0.2 g, 0.25 mmol) in dry THF (2 mL) under a nitrogen atmosphere, TBAF (0.4 mL, 0.38 mmol) was added and the mixture stirred for 3 h. The reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (2×10 mL). The organic layers were washed with water (2×10 mL), brine (10 mL) and dried ($Na_2SO_4$). The solvent was evaporated and the residue purified by column chromatography (60–120 Silica gel, 55 % EtOAc in petroleum ether) to furnish **1** (69 mg) in 87 % yield as a white solid.

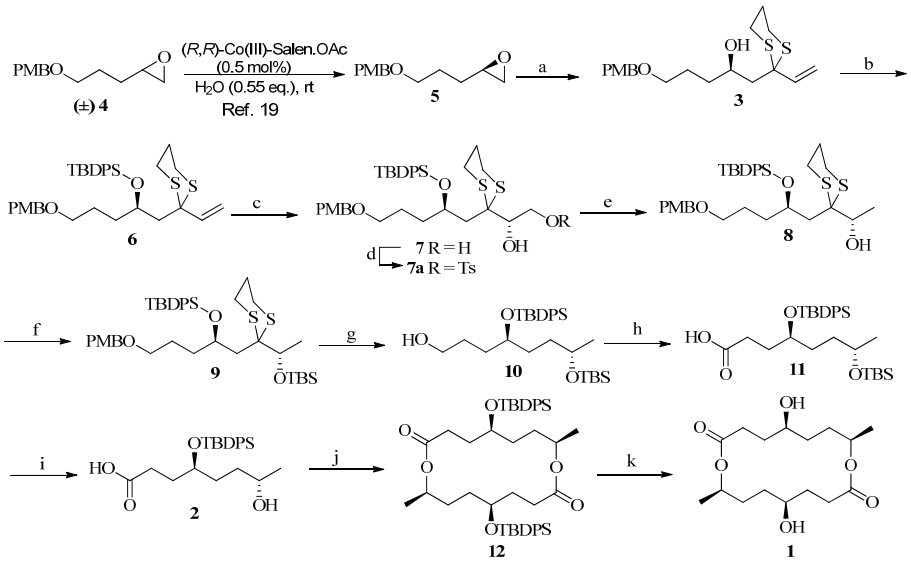
## RESULTS AND DISCUSSION

The retrosynthesis of **1** envisioned that it could be produced from the hydroxy-acid **2** *via* cyclodimerization under the Mitsunobu reaction conditions followed by deprotonation of silyl ethers. Hydroxy-acid **2** is the vital fragment could be attained by a short sequence involving Sharpless asymmetric dihydroxylation of alcohol **3** followed by reductive elimination using lithium aluminium hydride. The alcohol fragment **3** could be obtained from (±)-epoxide **4** through regioselective ring-opening with 2-vinyl-1,3-dithiane (Scheme 1).




Scheme 1. Retrosynthetic analysis of tetrahydropyrenophorol.

From the retrosynthetic analysis, it was envisaged that hydroxy acid **2** is the crucial fragment for the synthesis of tetrahydropyrenophorol. Consequently, the synthesis of the hydroxy acid segment **2** was instigated from the known (±)-epoxide **4** (Scheme 2), which was converted into enantiopure epoxide **5** using a literature protocol.[19]




*Reagents and conditions*. a) 2-vinyl-1,3-dithiane, *n*-BuLi, dry THF, –78 °C, 3 h, 81 %; b) TBDPSCl, imidazole, $CH_2Cl_2$, rt, 4 h, 79 %; c) AD-mix-β, *t*-BuOH/$H_2O$, 0 °C to rt, 32 h, 82 %; d) *p*-TsCl, $Bu_2SnO$, $Et_3N$, rt, 30 min; e) LAH, THF, 0 °C to rt, 3 h, 77 %; f) TBSCl, imidazole, $CH_2Cl_2$, rt, 3 h, 81 %; g) Raney Ni, EtOH, 80 °C, 4 h, 78 %; h) TEMPO, BIAB, *aq* $CH_2Cl_2$, 0 °C, 2 h, 75 %; i) PPTS, EtOH, 50 °C, to rt, 3 h, 91 % j) $Ph_3P$, DEAD, toluene:THF (10:1) –25 °C, 10 h, 56 %; k) TBAF, THF, 0 °C to rt, 3 h, 87 %.

Scheme 2. Synthesis of (–)-tetrahydropyrenophorol.

After having the requisited epoxide **5** that upon regioselective ring-opening with 2-vinyl-1,3-dithiane in the presence of *n*-BuLi in dry THF at –78 °C for 3 h

provided alcohol **3** in 81 % yield, which on ensuing silylation with TBDPSCl gave silyl ether **6** in 79 % yield. Next, the terminal olefin in silyl ether **6** was then subjected to Sharpless asymmetric dihydroxylation[14,20] with AD-mix-$\beta$, affording diol **7** (dr 9:1) in 82 % yield. The diastereomeric ratio was assigned based on the crude $^1$H-NMR spectrum of **7** (Supplementary material). The mechanism of the sharpless dihydroxylation originates through the generation of $OsO_4$–ligand complex. The alkene on cycloaddition with the osmium complex creates the cyclic intermediate and upon basic hydrolysis liberates the requisite diol. The ligand in AD-mix-$\beta$ ($(DHQD)_2PHAL$ used as chiral ligand) accelerates the reaction and transfers the chirality.[21,22]

Monotosylation of diol **7** was attained with tosyl chloride in the presence of $Bu_2SnO$ and $Et_3N$ in $CH_2Cl_2$ furnishing the corresponding primary tosylate **7a** in quantitative yield. Next, tosylate **7a** was subjected to reductive elimination using lithium aluminium hydride in dry THF, producing the secondary alcohol **8** in 77 % yield. Subsequent silylation with TBSCl and imidazole in $CH_2Cl_2$ gave **9** in 81 % yield. In the next stage, the dithiane moiety and PMB group in compound **9** were removed in a single step using Raney Ni[23] to provide alcohol **10** in 78 % yield.

The resulting alcohol **10** was then treated with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and [bis(acetoxy)iodo]-benzene (BAIB)[24] in aq. $CH_2Cl_2$ at 0 °C to room temperature for 2 h to obtain the desired acid **11** in a single step. Selective desilylation of **11** with PPTS in ethanol afforded hydroxy acid **2** in 91 % yield.

After completion of the synthesis of fragment **2**, the focus shifted to macrolactonization and further transformations to complete the synthesis of the target compound. Accordingly, hydroxy-acid **2** on cyclodimerization under standard Mitsunobu conditions[25] ($Ph_3P$ and DEAD) at –25 °C for 10 h furnished **12** in 56 % yield. Desilylation of **12** with TBAF in dry THF achieved (–)-tetrahydropyrenophorol **1** in 87 % yield, the spectral and optical rotation data were comparable with reported data.[12]

## CONCLUSIONS

In the study, total synthesis of (–)-tetrahydropyrenophorol macrodiolide was consummated in a simple and divergent way starting from racemic epoxide. Sharpless asymmetric dihydroxylation and Mitsunobu cyclodimerization were used as typical reactions. Good yields, smaller number of steps, and readily available materials are the salient features of the synthetic approach. The syntheses of related macrodiolides are underway in our laboratory and will be reported in due course.

## SUPPLEMENTARY MATERIAL

$^1$H- and $^{13}$C-NMR spectra and spectral data for the synthesized compounds are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/index, or from the corresponding author on request.

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ИЗВОД

## СТЕРЕОСЕЛЕКТИВНА СИНТЕЗА (–)-ТЕТРАХИДРОПИРЕНОФОРОЛА

VYASABHATTAR RAMANUJAN, SHAIK SADIKHA и CHEBOLU NAGA SESHA SAI PAVAN KUMAR

*Division of Chemistry, Department of Sciences and Humanities, Vignan's Foundation for Science, Technology & Research (VFSTR) University, Vadlamudi, Guntur 522 213, Andhra Pradesh, India*

Тетрахидропиренофорол је занимљив макролид изолован из биљке *Fagonia cretica*. Тотална синтеза (–)-1-тетрахидропиренофорола је постигнута на елегантан и линеаран начин из лако доступног рацемског епоксида. Поступак укључује реакције региоселективног отварања епоксида, Шарплесове асиметричне дихидроксилације и Мицунобу циклодимеризације да би био формиран 16-члани бис-лактонски прстен. Описан синтетички приступ је једноставан и може бити коришћен за синтезу сродних једињења на економичан и високо стереоселективан начин.

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