SHORT PAPER

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Facile enantioselective synthesis of 6*R*-(+)-goniothalamin and (6*R*, 7*R*, 8*R*)-(+)-goniothalamin oxide†

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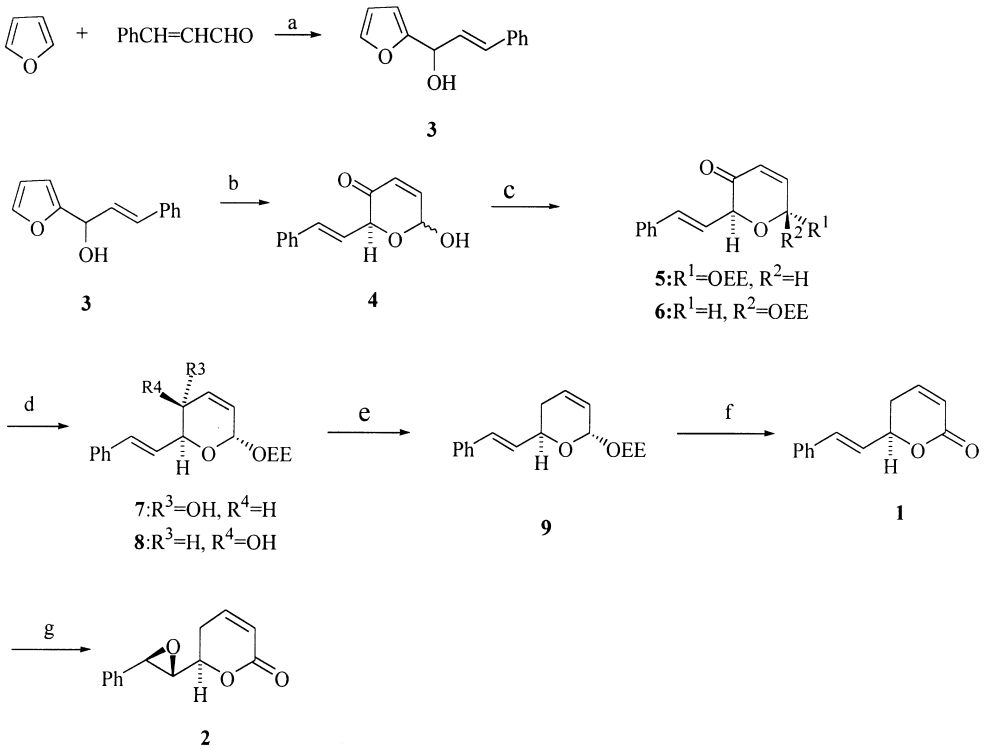
Facile enantioselective total syntheses of 6*R*-(+)-goniothalamin **1** and (6R, 7R, 8R)-(+)-goniothalamin oxide **2** were achieved through the Sharpless kinetic resolution of racemic secondary 2- furylmethanol **3** in a short synthetic route.

Keywords: 6*R*-(+)-goniothalamin, (6*R*, 7*R*, 8*R*)-(+)-goniothalamin oxide, Sharpless kinetic resolution.

6*R*-Goniothalamin **1**[1,2] (Fig. 1) and (6*R*, 7*R*, 8*R*)-(+)-goniothalamin oxide **2**[3,4] (Fig. 1) have been isolated from *Goniothalamus macrophyllus* as the active embryotoxic and teratogenic components. The configuration of goniothalamin oxide **2** was established by chemical transformations and single crystal X-ray crystallography as (6*R*, 7*R*, 8*R*).[5] Owing to the interesting biological activity of 6-substituted 5,6-dihydro-2H-pyran-2-ones, and also in order to determine their absolute configuration, these natural products have been synthesised in their optically active forms by a number of chemists.[6-9] As part of our continuing work on the synthesis of physiologically active natural products, we successfully synthesised 6*R*-(+)-goniothalamin **1** and (6*R*, 7*R*, 8*R*)-(+)-goniothalamin oxide **2** by using the Sharpless kinetic resolution of racemic secondary 2-furylmethanol **3**[10,11] to provide a facile synthetic route.

Our synthetic strategy was based on the kinetic resolution of racemic secondary 2-furylmethanol **3** with the Sharpless reagent.[10,11] By the Sharpless kinetic resolution, we were able to prepare the optically active pyranone **4** as a key intermediate compound for the synthesis of the target natural products.

The synthesis of 6*R*-(+)-goniothalamin **1** and (6*R*, 7*R*, 8*R*)-(+)-goniothalamin oxide **2** is shown in Scheme 1. The kinetic resolution of compound **3** was performed with *t*-butyl hydroperoxide (TBHP) (0.6mol equiv.) and a catalytic amounts of L- (+)-diisopropyl tartrate (L-DIPT) (30mol%) and titanium tetraisopropoxide [Ti ($O^iPr)_4$] (20mol%) in anhydrous CH_2Cl_2 in the presence of molecular sieves 4Å at –30– –40°C. The reaction mixture was stirred for 24h under an atmosphere of argon to afford the pyranone **4** in 35% yield.[10,11] Protection of the lactol **4** with ethyl vinyl ether gave



Scheme 1
Reagents and conditions: (a) BuLi, THR, –78°C; (b) L-(+)-DIPT, Ti(O-^{i}Pr)$_4$, TBHP, CH_2Cl_2 –25°C; (c) Ethyl vinyl ether, PPTS, CH_2Cl_2, r. t; (d) $NaBH_4$, $CeCl_3$. $7H_2O$, MeOH, –30– –40°C; (e) (1) Et_3N, DMAP, CH_3SO_2Cl, CH_2Cl_2, 0°C; (2) $LiAlH_4$, THF, 50°C, (f) CrO_3/HOAc, r. t; (g) m-CPBA, CH_2Cl_2, r. t.

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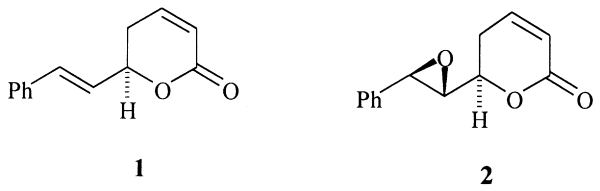

1 **2**

Figure 1

the α- and β-ethoxyethyl ethers **5** and **6** in 74% and 10% yield respectively. Reduction of compound **5** with $NaBH_4$ and $CeCl_3.7H_2O$ in MeOH at –30– –40°C furnished the allyl alcohols **7** and **8** in 78% and 4.0% yield respectively.[12] The stereochemistry of the hydroxy group in compound **7** could not be established at this stage; however, it was assumed to be 3*R* based on the results of similar works by Sammes *et al*.[13] The alcohol **7** was deoxygenated by successive methanesulfonylation without purification and lithium aluminium hydride reduction of the mesylate to afford compound **9**. Finally oxidation of the compound **9** with Jones reagent gave 6*R*-(+)-goniothalamin **1**, m.p. 78–80°C, (lit.[1] 81–82°C); $[\alpha]_D^{20}$ +163.8 (c 1.12, $CHCl_3$), {lit.[1] $[\alpha]_D$ +170.3 (c 1. 38, $CHCl_3$)}, Oxidation of **1** with *m*-CPBA yielded the natural compound **2** and its (6*R*, 7*S*, 8*S*) isomer (3:2). m.p. 91–92°C, $[\alpha]_D^{20}$+94.7 (c 0.62, $CHCl_3$), {lit.[3] m.p. 90–94°C, $[\alpha]_D$ +100.7 (c 0.7,$CHCl_3$)} The above data are in agreement with literature values.[1-5]

In summary, we have successfully applied the Sharpless kinetic resolution of furylmethanol **3** by employing the Sharpless reagent to the enantioselective synthesis of 6*R*-(+)-goniothalamin **1** and (6*R*, 7*R*, 8*R*)- (+)-goniothalamin oxide **2** by a facile synthetic route.

Experimental

The melting points were measured with a X-4 apparatus. IR spectra were recorded on a Nicolet 170 SXFT-IR spretrometer. The ^1H NMR data in $CDCl_3$ solution were recorded on a Brucker AM-400 MHz spectrometer. The chemical shifts are reported in ppm relative to TMS. Mass spectra were measured with a ZAB-HS mass spectrometer (EI) by direct inlet at 70 eV, and signal are given in *m/z* with relative intensity (%) in backets. Optical rotation meacurements were carried out on a JASCO 20C polarimeter with 0.2 dm tube. All solvents were freshly purified and dried by standard techniques prior to use. Purification of products was performed by flash column chromatography on silica gel (200–300 mesh) purchased from Qing Dao Marine Chemical Co. (Qingdao, China) and eluting with a solvent mixture (v/v) of petroleum ether (60–90°C) (bp) and ethylacetate (EA). Perparative T.L.C was performed on a glass plate (20×20 cm) coated with GF_{254} purchased from Qing Dao Marine Chemical Co. (Qingdao, China), and the compounds were extracted with CH_2Cl_2 or AcOEt.

1-(2-furyl) cinnamyl alcohol (**3**): To a solution of 2-lithium furan [prepared from furan (16 ml, 0.22 mol) and 2.4M BuLi (80 ml, 0.192 mol) in THF (80 ml) at –78°C] was added slowly a solution of (E)–cinnamaldehyde (16.5 ml, 0.132 mmol) in THF (30 ml) and the reaction mixture was stirred for 30 mins under an atmosphere of Ar. After addition of brine (30 ml), the mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (6:1) as eluant to afford the furyl alcohol **3** (25.6 g, 97%) as a red oil; ν_{max} (KBr) /cm^{-1} 3360, 1640, 3020; *m/z* (EI) 200 (M^+), 182, 115, 102, 77, 68; δ_H (400MHz, $CDCl_3$) 2.19–2.35 (1H, br s, OH), 5.42 (1H, d, *J* 6.2Hz, CHOH), 6.33 (1H, d, *J* 3.8Hz, 3-H), 6.38 (1H, dd, *J* 3.8 and 1.9 Hz, 4-H), 6.48 (IH, dd, *J* 15.8 and 6.2Hz, CH=CHPh), 6.75 (1H, d, *J* 15.8Hz, CH=CHPh), and 7.15–7.45 (6H, m, 5-H and Ph). (Found: C, 77.9; H, 6.1. $C_{13}H_{12}O_2$ requires C, 78; H, 6%)

(2S)-6-Hydroxy-2- [(E)-styryl]-6H-pyran-3(2H)-one (**4**): To a solution of the furyl alcohol **3** (11 g, 55 mmol) and L-DIPT (1.93 g, 8.25 mmol) in anhydrous CH_2Cl_2 (120 ml) at room temperature was added activated molecular sieves $4A^0$ (1.84 g) under an atmosphere of Ar. The stirred mixture was cooled to –30°C, treated with $Ti(O^iPr)_4$ (1.57 g, 5.5 mmol), and stirred for 30 min at –30°C. The reaction mixture it was treated with TBHP (5.0–6.0M, in solution in nonane, 5.5 ml, 27.5 mmol) and it was then stirred for 24h at the same temperature. A freshly prepared solution of $FeSO_4.7H_2O$ (4.62 g, 16.6 mmol) and tartaric acid (16.6 g, 110 mmol) in deionised water (30 ml) was added to the reaction mixture at –30°C. The resulting mixture was stirred at room temperature until the mixture was clear. The organic layer was separated and washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether – ethyl acetate (4:1) as eluant to afford to afford the pyranone **4** (3.85 g, 35 %) as a brown oil; $[\alpha]_D^{20}$ +126.3 (c 0.5, CHCl3); ν_{max} (KBr)/cm^{-1} 3350, 1720, 1680, 1640; *m/z* (EI) 216 (M^+), 198, 131, 115, 84, 77; δ_H (400MHz, $CDCl_3$) 3.8–4.2 (1H, br s, OH), 4.80 (0.2H, d, *J* 5.9 Hz, 2-H), 5.26 (0.8H, dd, *J* 5.7 and 1.5 Hz, 2-H), 5.77 (1H, br s, 6-H), 6.18 (1H, dd, *J* 10.3 and 1.5Hz, 4-H), 6.39 (0.8H, dd, *J* 15.8 and 5.72 Hz,CH=CHPh),6.48 (0.2H, dd, *J* 15.8 and 6.3 Hz, CH=CHPh), 6.75 (1H, dd, *J* 15.8 and 1.9 Hz, CH=CHPh), 6.95 (0.8H, dd, *J* 10.3 and 3.3 Hz, 5-H), 6.98 (0.2H, dd, *J* 10.3 and 1.9 Hz, 5-H) and 7.25–7.45 (5H, m, Ph). (Found: C, 72.4; H, 5.57. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.56%).

(2S, 6S)- and (2S, 6R) -6-(1-Ethoxyethoxy)-2-[(E)-styryl]-6H-pyran-3(2H)-one (**5**) *and* (**6**): To a solution of the lactol **4** (3.5 g, 16.2 mmol) in CH_2Cl_2 (20 ml) were added ethyl vinyl ether (11.7 g, 162 mmol) and a catalytic amount of pyridium toluene-*p*-sulfonate at room temperature. The reaction mixture was stirred for 3h at room temperature and poured into water (30 ml). The mixture was extracted with CH_2Cl_2 (100 ml). The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (12:1) as eluant. The first fraction gave the α-anomer **5** (3.2g, 74%) as yellow oil. $[\alpha]_D^{20}$ +5.6 (c 0.15, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3040, 1720, 1680, 1640; *m/z* (EI) 243 (M^+-45), 216, 198, 131, 115, 103, 84, 77; δ_H (400MHz, $CDCl_3$) 1.22 and 1.25 (3H, each t, *J* 7.2 Hz, CH2Me), 1.43 and 1.45 (3H, each d, *J* 4.8 Hz, CHMe), 3.55–3.75 (2H, m, OCH_2Me), 5.01 and 5.11 (1H, each q, *J* 5.3Hz,OCHMe), 5.12 and 5.22 (1H, each dd, *J* 5.4 and 1.7 Hz, 2-H), 5.62 and 5.66 (1H,each d, *J* 3.5 Hz, 6-H), 6.15 and 6.18 (1H, each d, *J* 10.3 Hz), 4-H), 6.40 and 6.45 (1H, each dd, *J* 15.6 and 5.6 Hz, CH=CHPh), 6.73 (1H, d, *J* 15.6 Hz, CH=CHPh), 6.90 and 6.92 (1H, each dd, *J* 9.9 and 3.4 Hz,5-H) and 7.25–7.45 (5H, m, Ph). (Found: C, 70.86; H, 6.92. $C_{17}H_{20}O_4$ requires C, 70.83; H, 6.94%).

The second fraction gave the β-anomer **6** (1.3g, 10%) as a yellow oil. $[\alpha]_D^{20}$ +19.6 (c 0.15, $CHCl_3$); δ_H (400MHz, $CDCl_3$) 1.19 and 1.25 (3H, each t, *J* 7.2 Hz, CH_2Me), 1.38 and 1.45 (3H, each d, *J* 5.0 Hz, CHMe), 3.35–3.75 (2H, m, OCH_2Me), 4.82 and 4.98 (1H, each d, *J* 6.5 Hz, 2-H), 5.01 and 5.13 (1H, each q, *J* 6.3Hz,OCHMe), 5.64–5.76 (1H, m, 6-H), 6.13–6.28 (1H, m, 4-H), 6.44 and 6.65 (1H, each dd, *J* 15.6 and 6.6 Hz, CH=CHPh), 6.70 and 6.73 (1H, each d, *J* 15.6 Hz, CH=CHPh), 6.90 and 6.95 (1H, each dd, *J* 9.9 and 3.4 Hz, 5-H) and 7.25–7.45 (5H, m, Ph).

(2S, 3R, 6S)- and (2S, 3S, 6S) -6-(1-ethoxyethoxy)-2-[(E)-styryl]-3,6-dihydro-2H-pyran-3-ol (**7**) *and* (**8**): To a stirred solution of the enone **5** (3.5 g, 12.2 mmol) and $CeCl_3.7H_2O$ (4.52 g, 12.2 mmol) in MeOH (40ml) at –30– –40°C was added the powder of sodium borohydride (0.464 g, 12.2 mmol). The reaction mixture was stirred for 1h at the same temperature. After dilution with brine (30 ml) the mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (5:1) as eluant. The first fraction gave the compound **7** (2.25 g, 78%), $[\alpha]_D^{20}$ –31.2 (c 0.2, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3434, 1640, 1600; *m/z* (EI) 228(M^+-72), 176, 151, 131, 115, 103, 77; δ_H (400MHz, $CDCl_3$) 1.18 and 1.23 (3H, each t, *J* 7.2Hz, CH2Me), 1.36 and 1.38 (3H, each d, *J* 5.7 Hz, CHMe), 1.86–1.92 (1H, br s, OH), 3.48–3.73 (2H, m, OCH2Me), 4.08–4.10 (1H, br s, 3-H), 4.27 and 4.33 (1H, each dd, *J* 9.2 and 6.7 Hz, 2-H), 4.93 and 5.0 (1H, each q, *J* 5.4 Hz, OCHMe), 5.26 and 5.35 (1H, each br s, 6-H), 5.73 and 5.81 (1H, each dt, *J* 11.2 and 2.4, 5-H), 6.0 (1H, dd, *J* 10.1 and 1.2 Hz, 4-H), 6.32 (1H, ddd, *J* 16.1 and 6.5, 3.1 Hz, CH=CHPh), 6.74 (1H, d, *J* 16.1 Hz, CH=CHPh) and 7.25–7.43 (5H, m, Ph). (Found: C, 70.32; H, 7.60. $C_{17}H_{22}O_4$ requires C, 70.34; H, 7.59%).

The second fraction gave the compound **8** (0.14 g, 4 %). $[\alpha]_D^{20}$ –14.7 (c 0.2, $CHCl_3$); δ_H (400MHz, $CDCl_3$) 1.16 and 1.23 (3H, each t, *J* 7.4Hz, CH_2Me), 1.36 and 1.38 (3H, each d, *J* 5.8 Hz, CHMe), 1.90–2.10 (1H, br s, OH), 3.46–3.82 (2H, m, OCH_2Me), 4.05–4.12 (1H, br s, 3-H), 4.25 and 4.31 (1H, m, 2-H), 4.92 and 5.0 (1H, each q, *J* 5.3 Hz, OCHMe), 5.35 (1H, br s, 6-H), 5.82 and 5.85 (1H, each

t, *J* 2.3Hz, 5-H), 6.04 (1H, d, *J* 10.5 Hz, 4-H), 6.32 (1H, dd, *J* 16.2 and 6.7 Hz, CH=CHPh), 6.76 (1H, d, *J* 16.2 Hz, CH=CHPh) and 7.25–7.45 (5H, m, Ph).

(2S, 6R) -2-(1-Ethoxyethoxy)-6-[(E)-styryl]-2, 6-dihydro-2H-pyran (**9**): To a stirred solution of the alcohol **7** (500 mg, 1.724 mmol) in anhydrous CH_2Cl_2 (10 ml) were added triethylamine (0.72 ml, 5.16 mmol), a catalytic amount of 4-N,N-dimethylaminopyridine and methanesulfonyl chloride (0.3 ml, 3.44 mmol) at 0°C under an argon atmosphere. Stirring was continued for 1h at the same temperature. After addition of brine, the mixture was extracted with CH_2Cl_2 (30 ml), and the organic layer was dried over Na_2SO_4 and evaporated to give the crude mesylate, which was relatively unstable. The mesylate was used for the next reaction without purification. To a stirred suspension of lithium aluminum hydride (196 mg, 5.16 mmol) in anhydrous THF (10 ml) was added a solution of the mesylate in anhydrous THF (15 ml) at 0°C and the reaction mixture was stirred for 6h at 50°C under an argon atmosphere. After addtion of saturated aqueous sodium hydroxide solution, the mixture was stirred for 30 mins and white precipitate was filtered off. The filtrate was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (20:1) as eluant to afford compound **9** (308 mg, 65%) as a colourless oil. $[\alpha]_D^{20}$ +93 (c 0.30, $CHCl_3$); ν_{max} (KBr)/cm^{-1} 1680, 1640; *m/z* (EI) 229 (M^+-45), 185, 167, 155, 115, 103, 77; δ_H (400MHz, $CDCl_3$) 1.21 and 1.24 (3H, each t, *J* 7.2Hz, CH_2Me), 1.41–1.43 (3H,m, CHMe), 2.12–2.25 (2H, m, 5-H), 3.53–3.74 (2H, m, OCH_2Me), 4.58 (1H, m, 2-H), 4.96 and 5.03 (1H, each q, *J* 5.6 Hz, OCHMe), 5.27 and 5.37 (1H, each br s, 6-H), 5.75–5.81 (1H, m, 3-H), 6.09 (1H, m, 4-H), 6.27 (1H, dd, *J* 16.2 and 5.9 Hz, CH=CHPh), 6.65 (1H, d, *J* 16.2 Hz, CH=CHPh) and 7.25–7.43 (5H, m, Ph). (Found: C, 74.43; H, 8.04. $C_{17}H_{22}O_3$ requires C, 74.45; H, 8.03%).

6R-Goniothalamin (**1**): To a solution of the lactol **9** (200 mg, 0.73 mmol) in HOAc (5 ml) was added the solution of CrO_3 (150mg)/HOAc (7ml). The reaction mixture was stirred for 4h at room temperature. The mixture was poured into water (10 ml) and extracted with CH_2Cl_2 (30 ml). The organic layer was washed with brine and saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum ether–ethyl acetate (6:1) as eluant to afford the lactone **1** (105 mg, 72 %). as an amorphous solid. m.p. 78–80°C, (lit. 1 81–82°C); $[\alpha]_D$ +163.8 (c 1.12, $CHCl_3$), {lit.[1], $[\alpha]_D$ +170.3 (c 1.38, $CHCl_3$). ν_{max} (KBr)/cm^{-1} 1720, 1680, 1240; *m/z* (EI) 200 (M^+), 172, 131, 115, 104, 91, 77; δ_H (400MHz, $CDCl_3$) 2.47 (2H, m, 5-H), 5.01 (1H, m, 6-H), 6.03 (1H, dt, *J* 10.2 and 2.4Hz, 3-H), 6.23 (1H, dd, *J* 15.8 and 5.8 Hz, CH=CHPh), 6.72 (1H, dd, *J* 15.8 and 1.8 Hz, CH=CHPh), 6.86 (1H, dt, *J* 10.2 and 3.8 Hz, 4-H), 7.25-7.43 (5H, m, Ph); ^{13}CNMR (400MHz, $CDCl_3$) 164 (C-2), 145 (C-4), 136 (C-9), 134 (C-8), 129 (C-11 and C-13), 128 (C-12), 127 (C-10 and C-14), 125 (C-7), 122 (C-3), 78 (C-6), 30 (C-5). (Found: C, 78.12; H, 5.96. $C_{13}H_{12}O_2$ requires C, 78; H, 6%). Its spectroscopic data is identical with those reported.[1,2]

(6R, 7R, 8R)-Goniothalamin oxide (**2**): To a stirred solution of **1** (80 mg, 0.4 mmol) in CH_2Cl_2 (10 ml), *m*-CPBA (138 mg, 0.8 mmol) was added at room temperature. The reaction mixture was stirred for 60h at room temperature. The reaction mixture was quenched with 20% aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with petroleum–ethylacetate (5:1) as eluant to afford the mixture of (6*R*, 7*R*, 8*R*)-goniothalamin oxide **2** (65 mg, 52%) and (6*R*, 7*S*, 8*S*)/(+)-isogoniothalamin oxide (3:2). The mixture was separated by preparative TLC (petroleum ether/ethyl acetate 4:1) to afford (6*R*, 7*R*, 8*R*)-goniothalamin oxide **2**. m.p. 91–92°C, (lit.3, 90–94°C); $[\alpha]_D$ +94.7 (c 0.62, $CHCl_3$), {lit.[3], $[\alpha]_D$ +100.7 (c 0.7, $CHCl_3$)}. *m/z* (EI) 216 (M^+), 200, 154, 148, 131, 97, 77, 69. δ_H (400MHz, $CDCl_3$) 2.45 (2H, m, 5-H), 3.25 (1H, dd, *J* 5.8 and 1.8 Hz, 7-H), 3.88 (1H, d, *J* 1.8 Hz, 8-H), 4.50 (1H, *J* 5.4 and 7.4 Hz, 6-H), 6.05 (1H, dt, *J* 9.5 and 1.8 Hz, 3-H), 6.95 (1H, dt, *J* 9.5 and 4.8 Hz, 4-H), 7.3–7.45 (5H, m, Ph); ^{13}CNMR (400MHz, $CDCl_3$) 163 (C-2), 145 (C-4), 136 (C-9), 130 (C-11, C-12 and C-13), 127 (C-10 and C-14), 122 (C-3), 77 (C-6), 62 (C-8), 58 (C-7), 25 (C-5). (Found: C, 72.18; H, 5.57. $C_{13}H_{12}O_3$ requires C, 72.22; H, 5.56%). The spectroscopic data are identical with those reported.[3,5]

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References

1 J. Rhlubucek and A.V. Robertson, *Aust.J.chem.* 1967, **20**, 2199.
2 J.R. Jewers, J.B. Davis, J. Dougan, A.H. Manchanda, G. Blunden, A. Kyi and S. Wetchapinan, *Phytochemistry*, 1972, **11**, 2025.
3 T.W. Sam, C.S. Yeu, S. Matsjeh, E.K. Gan, D. Razak, A.L. Mohamed, *Tetrahedron letters*, 1987, **28**, 2541.
4 F. Bennett, D. W. Knight, G. Fenton, *J. Chem. Soc. Perkin Trans 1*, 1991, 519.
5 S.H. Goh, G.C.L. Ee, C.H. Chuah, C. Wei, *Aust. J. Chem.*, 1995, **48**, 199.
6 T. Honda, T, Kametani, K. Kanai, Y. Tatsuzaki, M. Tsubuki, *J. Chem. Soc. Perkin Trans 1* 1990, 1773.
7 B. Connor, G. Just, *Tetrahedron Lett*. 1986, **27**, 529.
8 S. Kazutoshi, I. Yasuhiro, H. Tomiki, *Tetrahedron Lett*. 2000, **11**, 4529.
9 A.M. Hmez, L.U. eatriz, V. Serafin, J. Ritobal, *Chem. Commun*. 1997, 1647
10 M. Kusakabe, Y. Kitano, Y. Kobayaashi and F. Sato, *J. Org. Chem*., 1989, **53**, 1586.
11 Y. Gao, R.M. Hanson, J.M. Klunder, S.Y. Ko, H, Masamune, K.B. Sharpless, *J. Am. Chem. Soc*., 1987, **109**, 5765.
12 H. Toshi, T. Hironao, M. Shigehiro, T. Masayoshi, *Tetrahedron Lett*. 1993, **34**, 8275.
13 P.G. Sammes, D. Thetford, *J. Chem. Soc. Perkin Trans 1,* 1988, 111.