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Transformation of (+)-thiomicamine into the *p*-methylthio analogue of (+)-5-*epi*-cytoxazone

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Abstract—(2*S*,3*S*)-(+)-Thiomicamine **3**, a commercially available aminodiol, was transformed into (4*R*,5*S*)-5-hydroxymethyl-4-(*p*-methylthiophenyl)-2-oxazolidinone **10**, a compound related to cytoxazone-type biologically active natural products. The synthetic strategy of the highly regio- and stereoselective synthesis was based upon the reversal of the position of the hydroxyl and amine functionalities in **3**, accomplished via azidolysis of the key intermediate, epoxide **6**.

1. Introduction

More than 20 different syntheses of (−)-cytoxazone **1** and its stereoisomers, for example, **2** (Fig. 1) have been reported since the isolation of this cytokine modulator from *Streptomyces* sp. by Osada et al. in 1998.[1,2] The synthesis of (−)-cytoxazone and its congeners appears to be attractive to many research teams in view of the possibility of developing novel immunotherapeutic agents and also because the 4,5-disubstituted 2-oxazolidinone ring system provides an interesting objective for various asymmetric synthesis strategies.

Since the oxazolidinone ring is conveniently constructed from β-aminoalcohols, in all the syntheses performed so far, efforts have been made to prepare these key intermediates in high enantiomeric purity. This has been accomplished in two ways: either by the enantioselective introduction of hydroxy and amino functionalities into prochiral cinnamic acid derivatives or by the construction of the carbon framework by formation of a carbon–carbon bond between two building blocks, chiral pool approach included.

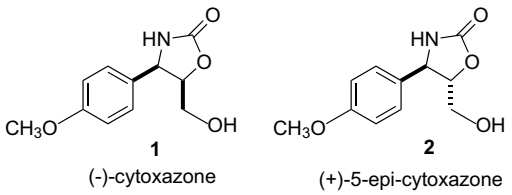

Figure 1.

In syntheses in which *E*-*p*-methoxycinnamic acid derivatives such as esters, amides or cinnamic alcohol were used as substrates, the 2-hydroxy-3-amino functionalities were introduced either via a two-step procedure, involving catalytic asymmetric Sharpless dihydroxylation followed by azidolysis[3–5] or straightforwardly, by Sharpless aminohydroxylation.[6] A one-pot amidation/oxidation[7] or epoxidation/azidolysis[8] process was applied to the cinnamic acid derivatives as well. Racemic cytoxazone *rac*-**1** and 4-*epi*-cytoxazone *rac*-**2** were also prepared from methyl *p*-methoxyphenyl glycidate and resolved by enzymatic methods.[9]

The C–C bond forming methodology, which relies on the chiral pool approach, uses commercially available amino acids[10,11] and carbohydrates[12,13] as substrates. Homologation can then be achieved by the addition of Grignard reagents[10,12,13] or cyanohydrin formation[11] via the corresponding aldehydes. The aldol-type reaction was also successfully applied in C–C bond forming methodology. Thus, *p*-methoxybenzylidene amines, both chiral[14,15] and prochiral,[16,17] were treated with carbon nucleophiles in diastereoselective[14,15,17] and enantioselective [16] syntheses. A diastereoselective aldol reaction followed by Curtius rearrangement[18,19] and the diastereoselective imino 1,2-Wittig rearrangement of hydroximates[20–22] were another way of the synthesis of β-aminoalcohols.

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To complete the synthesis of cytoxazone **1** and its congeners the prepared chiral β-aminoalcohols were then subjected to standard functional group manipulations, including cyclization either of the *N*-Boc derivatives or directly from aminoalcohols and phosgene equivalents.

Herein we report another approach to the synthesis of cytoxazone derivatives. It is based upon (+)-thiomicamine **3**, 2-amino-1-(4-methylthiophenyl)-1,3-propanediol, which is a commercially available industrial waste product. (+)-Thiomicamine **3** was used as the substrate and transformed into (+)-**10**, the *p*-methylthio analogue of (+)-5-*epi*-cytoxazone **2**, in a highly stereoselective synthesis in 44% overall yield, involving a seven-step reaction sequence. The synthetic strategy applied is summarized in Scheme 1.

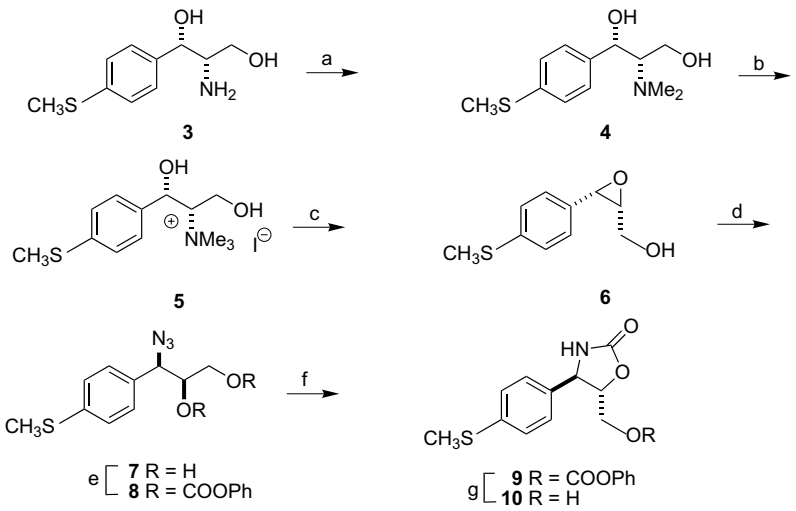
2. Results and discussion

In order for (+)-thiomicamine **3** to be used in the synthesis, the position of the amino and hydroxy groups had to be reversed. To achieve this, epoxide **6** was considered to be the key intermediate in the synthesis and was expected to be easily prepared by an (Scheme 1) intramolecular substitution of the amine function by the secondary hydroxyl group.

Therefore a straightforward procedure as described by Castedo et al.[23] was chosen, in which 2-amino-1-phenyl-1,3-propanediol was reacted with dichlorocarbene to give the corresponding epoxide in a simple operation. In our case, however, an inseparable mixture of products was formed. A two-step transformation of the primary amine into a good leaving group by its quaternization was undertaken. Thus, (+)-thiomicamine **3** was converted into methiodide **5** via *N*,*N*-dimethylthiomicamine **4** (mp 89.5–90.5 °C, $[\alpha]_D = +35.6$) prepared by refluxing **3** in a formic acid/formaldehyde mixture for 5 h, followed by N-methylation of **4** with methyl iodide in acetonitrile at room temperature for 18 h, to afford the quaternary salt **5** (mp 194–195.5 °C, $[\alpha]_D = +46.1$) in excellent yield. The next step of the synthesis, the formation of epoxide **6**, turned out to be very unreliable. It was strongly dependent upon the reaction conditions, in particular on the reaction temperature and the work-up procedure. Since the synthetic strategy undertaken was built up on the success of the epoxide formation step, several experiments were carried out to overcome this difficulty.

It was established that on treatment of a suspension of **5** in THF with an excess of sodium hydride in a strong stream of argon, it was very important to maintain the reaction temperature precisely at 65 °C, to prevent decomposition of the product. It was also important to cool the reaction mixture (ice-bath) immediately after the clear solution had formed (after ca. 2.5 h) and quench it with a sodium hydroxide/sodium chloride solution. Under these conditions, epoxide **6** (mp 77.5–79.0 °C, $[\alpha]_D = +41.6$) was produced in a quantitative yield. As expected, in the process of epoxidation, complete inversion of configuration at C-2 took place, giving epoxide **6** as a single diastereomer.[24] It should be noted that among the strategies applied for the asymmetric synthesis of cytoxazone and congeners, a related epoxide was used as the intermediate.[8]

For the regioselective introduction of the amine functionality into the benzylic position of various intermediates en route to cytoxazone or analogues, azidolysis with sodium azide in DMF,[25] dioxane,[9] acetonitrile[26] or acetone[13] was reported. Under these conditions however, long reaction times, elevated temperatures, and the presence of additives were often needed. Here, in this synthesis, excellent results were achieved when epoxide **6** in methoxyethanol/water (8:1) was reacted with (2.5:1) sodium azide/ammonium chloride[27] at 65 °C, affording azidodiol **7** (mp 92.0–93.5 °C, $[\alpha]_D = -200.2$) in high yield, as a single diastereomer.[24] Once again, an inversion of configuration took place at the second stereocenter, C-3.



Scheme 1. Reagents and conditions: (a) $HCOOH/CH_2O$ (85%); (b) CH_3I/CH_3CN (98%); (c) NaH/THF (99%); (d) $NaN_3/NH_4Cl/CH_3OCH_2CH_2OH$ (94%); (e) $ClCOOC_6H_5/PyH/CH_2Cl_2$ (90%); (f) $P(C_6H_5)_3/THF/H_2O$ (71%); (g) $K_2CO_3/CH_3OH/H_2O$ (88%).

With the position of the two functional groups reversed, the synthesis was then continued by treatment of azidodiol **7** with an excess of phenylchloroformate/pyridine in methylene chloride at ice-bath temperature to give dicarbonate **8** (oil, $[\alpha]_D$ −44.7), which was obtained in satisfactory yield. The construction of the 2-oxazolidinone ring was then performed in one-pot by treatment of **8** with triphenylphosphine in aqueous THF at 50 °C, during which the azide reduction and cyclization took place simultaneously. The desired 2-oxazolidinone carbonate **9** (mp 135.5–137.0 °C, $[\alpha]_D = +72.2$) was isolated in moderate yield as a single isomer.[24] Removal of the phenyloxycarbonyl group in **9** occurred via hydrolysis with potassium carbonate in aqueous methanol. The final product, (4*R*,5*S*)-(+)-5-hydroxymethyl-4-(*p*-methylthiophenyl)-2-oxazolidinone, (+)-**10** (mp 174.5–175.0 °C, $[\alpha]_D = +30.8$) was obtained as an enantiomerically pure compound[24] in 44% overall yield, based on (+)-thiomicamine **3**.

3. Conclusion

In conclusion, enantiomerically pure (4*R*,5*S*)-(+)-**10**, the sulfur analogue of (4*R*,5*S*)-(+)-5-*epi*-cytoxazone **2**, has been synthesized in 44% overall yield in seven steps starting from (+)-thiomicamine **3**. The key step of the synthesis, the reversal of the position of the hydroxyl and amine functional groups occurred via a highly stereo- and regioselective epoxidation/azidolysis process, involving inversion of configuration of both stereogenic centers.

It should be noted that in the synthesis described herein an industrial waste product has been used as a substrate and transformed into a compound related to natural products of potent biological activity.

4. Experimental

4.1. General methods

Melting points were determined on a Koffler block and are uncorrected. IR spectra: Bruker FT-IR IFS 113V. NMR spectra: Varian Gemini 300, with TMS as the internal standard. Mass spectra (EI): AM D402. Optical rotation: Perkin–Elmer polarimeter 242B. Elemental analysis: Vario EL III. Merck Kieselgel 60 (70–230 mesh) was used for column chromatography and Merck DC-Alufolien Kieselgel 60_{254} for TLC. Analytical HPLC: Waters HPLC system with Mallinkrodt–Baker Chiralcel OD-H column, hexane–isopropanol (9:1). (+)-Thiomicamine was purchased from Aldrich Chemical Co., and used as received.

4.2. (1*S*,2*S*)-2-Dimethylamino-1-(4-methylthiophenyl)-1,3-propanediol 4

A mixture of (+)-thiomicamine **3** (2.13 g, 10 mmol), formic acid (5 ml) and 37% aqueous formaldehyde (5 ml) was heated at reflux for 5 h. This was then cooled to room temperature rendered alkaline with 20% sodium hydroxide and stirred for 1 h, then extracted with ethyl ether until Dragendorff test was negative. The combined organic extracts were washed with water, dried, and concentrated under reduced pressure. The residue was dissolved in methanol/*iso*-propyl ether to give crystalline *N*,*N*-dimethylthiomicamine **4** in 85% yield. Mp 89.0–90.5 °C; $[\alpha]_D = +35.6$ (*c* 1.0, methanol). ^{1}H NMR ($CDCl_3$): δ ca. 1.7 (s, 1H, disappears on treatment with D_2O, OH), 2.47 (s, 3H, SCH_3), 2.51 (s, 6H, NCH_3), 2.64 (ddd, $J = 4.1$, 7.6, 9.8 Hz, 1H, H-2), 3.40 (dd, $J = 4.1$, 11.5 Hz, 1H, H-3), 3.51 (dd, $J = 7.6$, 11.5 Hz, 1H, H-3′), 4.35 (d, $J = 9.9$ Hz, 1H, H-1), ca. 4.50 (br s, 1H, disappears on treatment with D_2O, OH), 7.20–7.29 (m, 4H, Ar–H). MS *m*/*z* (%): 241 (M^+, <1), 178 (2), 151 (3), 137 (4), 109 (4), 91 (1), 89 (5), 88 (100). Found: C, 59.68; H, 8.62; N, 5.81; S, 13.24. $C_{12}H_{19}NO_2S$ (241.1) req.: C, 59.72; H, 7.94; N, 5.81; S, 13.26.

4.3. (1*S*,2*S*)-2-Dimethylamino-1-(4-methylthiophenyl)-1,3-propanediol methiodide 5

Compound **4** (1.75 g, 7.26 mmol) in acetonitrile (28 ml) and methyl iodide (2 ml) was stirred at room temperature for 20 h. The precipitate was filtered off, washed with ethyl ether and recrystallized from methanol to deposit methiodide **5** (2.7 g, 98%). Mp 195.5–196.5 °C; $[\alpha]_D = +46.1$ (*c* 0.98, methanol). ^{1}H NMR (DMSO-d_6): δ 2.48 (s, 3H, SCH_3), 3.15 (m, 1H, H-2), 3.36 (3s, 9H, NCH_3), 3.61 (m, 1H, H-3), 3.87 (m, 1H, H-3′), 5.12 (d, J = ca. 10 Hz, 1H, disappears on treatment with D_2O, CHO*H*), 5.39 (t, $J = 4.0$ Hz, 1H, disappears on treatment with D_2O, CH_2OH), 6.39 (d, $J = 3.6$ Hz, 1H, H-1), 7.29–7.40 (m, 4H, Ar–H). MS *m*/*z* (%): 193 (3), 152 (4), 151 (70), 142 (39), 137 (8), 127 (16), 110 (4), 89 (6), 88 (100). Found: C, 40,69; H, 5.96; N, 3.60; S, 8.29. $C_{13}H_{22}NO_2SI$ (383.0) req.: C, 40.72; H, 5.79; N, 3.67; S, 8.35.

4.4. (2*R*,3*S*)-2,3-Epoxy-3-(4-methylthiophenyl)-1-propanol 6

In a stream of argon, a suspension of methiodide **5** (0.76 g, 2 mmol) in tetrahydrofuran (80 ml) and sodium hydride (0.19 g, 8 mmol) was heated at 65 °C, while care was taken to keep the temperature at 65 °C itself. The moment of the solution became clear, ca. 2–2.5 h, the mixture was immediately cooled in ice-water bath and slowly treated with 10% sodium hydroxide containing 10% sodium chloride. The phases were separated and the organic phase concentrated under reduced pressure. The residue was partitioned between ethyl ether and 20% ammonium chloride, the organic layer separated, dried and the solvent evaporated to leave a TLC pure, pale-yellow precipitate (0.38 g, 99%, 100:0 dr[24]), which was used for the next step as such.

A sample was digested with benzene/hexane (1:1) giving **6** as a cream-colored solid. Mp 77.5–79.0 °C, $[\alpha]_D = +41.6$ (*c* 0.97, methanol). ^{1}H NMR (DMSO-d_6): δ 2.47 (s, 3H, SCH_3), 3.20–3.30 (m, 3H, H-2, H-1, H-1′), 4.13 (d, $J = 3.8$ Hz, 1H, H-3), 4.88 (t, $J = 4.9$ Hz, 1H, disappears on treatment with D_2O, CH_2OH), 7.20–7.37 (m, 4H, Ar–H). ^{1}H NMR (DMSO-d_6/D_2O): δ 2.46 (s, 3H, SCH_3), 3.22 (dd, J = ca. 7, 12.7 Hz, 1H, H-1), 3.33 (dd, $J = 4.3$, 12.7 Hz, 1H, H-1′), 3.29–3.34 (m, 1H, H-2), 4.16 (d, $J = 4.0$ Hz, 1H, H-3), 7.26–7.38 (m, 4H, Ar–H). ^{13}C NMR (DMSO-d_6): δ 14.61 (CH_3), 55.76 (CH), 58.29 (CH_2), 58.92, 125.54, 126.89 (CH), 131.82, 137.44 (C).

MS *m*/*z* (%): 196 (M^+, 100), 179 (26), 178 (52), 177 (22), 167 (31), 166 (66), 165 (62), 152 (22), 151 (48), 150 (24), 137 (67), 136 (31), 135 (77), 121 (61), 91 (38), 89 (26). Found: C, 61.17; H, 6.08; S, 16.20. $C_{10}H_{12}O_2S$ (196.1) req.: C, 61.20; H, 6.17; S, 16.31.

4.5. (2*S*,3*R*)-3-Azido-3-(4-methylthiophenyl)-1,2-propanediol 7

To a stirred solution of epoxide **6** (0.43 g, 2.2 mmol) in (8:1) 2-methoxyethanol/water (13.5 ml), sodium azide (0.72 g, 11 mmol) was added followed by ammonium chloride (0.23 g, 4.4 mmol) and the mixture was heated at 100 °C for 3 h. It was concentrated under reduced pressure and the residue extracted with ethyl ether. The organic extract was washed with 20% ammonium chloride, dried, and the solvent evaporated to deposit oily **7** (0.51 g, 98%, 97.8:2.2 dr[24]), that solidified on standing. After crystallization from methylene chloride–carbon tetrachloride, crystalline **7** in 94% yield and with 99.7:0.3 dr[24] was collected. Mp 92–93.5 °C; $[\alpha]_D = -200.2$ (*c* 0.98, methanol). IR (KBr) cm^{-1}: 3459, 3218 (br), 2107. ^1H NMR (DMSO-d_6): δ 2.48 (s, 3H, SCH_3), 3.19 (dd, $J = 5.5$, 11.0 Hz, 1H, H-1), 3.28 (dd, $J =$ ca. 5, 11.0 Hz, 1H, H-1′), 3.67 (m, 1H, H-2), 4.56 (d, $J = 5.9$ Hz, 1H, H-3), 4.70 (t, $J =$ ca. 5 Hz, 1H, disappears on treatment with D_2O, CH_2OH), 5.30 (d, $J = 5.6$ Hz, 1H, disappears on treatment with D_2O, $CHOH$), 7.20–7.34 (m, 4H, Ar–H). ^{13}C NMR ($CDCl_3$): δ 15.4 (CH_3), 62.63 (CH_2), 67.9, 74.8, 126.6, 128.0 (CH), 132.4, 139.7 (C). MS *m*/*z* (%): 239 (M^+, 23), 178 (22), 151 (38), 150 (100), 137 (13), 135 (19), 123 (19). Found: C, 50.21; H, 5.44; N, 17.57; S, 13.39. $C_{10}H_{13}N_3O_2S$ (239.1) req.: C, 50.19; H, 5.48; N, 17.57; S, 13.37.

4.6. (2*S*,3*R*)-3-Azido-1,2-diphenyloxycarbonyloxy-3-(4-methylthiophenyl)-propane 8

To a solution of azidodiol **7** (0.45 g, 1.86 mmol) in methylene chloride (15 ml), three portions each of a reagent composed of pyridine (0.15 ml, 1.8 mmol) and phenyl chloroformate (0.26 ml, 1.8 mmol) were added in 1 h intervals, at ice-bath temperature, with stirring. After reaching room temperature the reaction mixture was washed with 5% hydrochloric acid followed by 5% sodium hydroxide, dried, and the solvent evaporated under reduced pressure. The oily residue was chromatographed over silica gel (1:10) with carbon tetrachloride/methylene chloride (1:1) to give **8** as an oil (0.8 g, 90%); $[\alpha]_D = -44.7$ (*c* 0.86, methanol). IR (neat) cm^{-1}: 2107, 1765. ^1H NMR ($CDCl_3$): δ 2.50 (s, 3H, SCH_3), 4.02 (dd, $J = 5.2$, 12.3 Hz, 1H, H-1), 4.54 (dd, $J = 3.0$, 12.3 Hz, 1H, H-1′), 4.87 (d, $J = 8.5$ Hz, 1H, H-3), 5.21 (ddd, $J = 3.0$, 5.2, 8.5 Hz, 1H, H-2), 7.04–7.16 (m, 14H, Ar–H). MS *m*/*z* (%): 479 (M^+, 9), 220 (21), 178 (28), 176 (23), 164 (21), 150 (100), 135 (11), 123 (13), 94 (20), 77 (64). HRMS (M^+) found: 479.11219. $C_{24}H_{21}N_3O_6S$ req.: 479.11511.

4.7. (4*R*,5*S*)-4-(4-Methylthiophenyl)-5-phenyloxycarbonyloxy-2-oxazolidinone 9

To azido dicarboxylate **8** (0.48 g, 1 mmol) in tetrahydrofuran (10 ml) and water (0.2 ml), triphenylphosphine (0.79 g, 3 mmol) was added and the mixture heated at 50 °C for 1 h under an argon atmosphere. The solvent was evaporated and the wet residue extracted with ethyl ether. The organic solution was washed with 5% sodium hydroxide, 5% hydrochloric acid, and 20% ammonium chloride, dried and the solvent removed under vacuum. The oily residue was heated at reflux with *iso*-propyl ether (ca. 35 ml) until a clear solution was obtained. After cooling, the solid (0.29 g) was recrystallized two times from methanol to give enantiomerically pure[24] oxazolidinone **9** (0.14 g). An additional amount of **9** (0.13 g; total yield 71%) was recovered after column chromatography (silica gel 1:10, methylene chloride) of the mother liquor. Mp 135.5–137.5 °C, $[\alpha]_D = +72.2$ (*c* 0.64, methanol). IR (KBr) cm^{-1}: 3257, 1760, 1726. ^1H NMR (DMSO-d_6): δ 2.47 (s, 3H, SCH_3), 4.40–4.56 (m, 3H, CH_2, H-5), 4.75 (d, $J = 6.0$ Hz, 1H, H-4), 7.23–7.48 (m, 10H, Ar–H). MS *m*/*z* (%): 359 (M^+, 11), 277 (12), 222 (43), 221 (14), 179 (12), 178 (44), 174 (18), 165 (13), 151 (23), 150 (15), 132 (12), 94 (100), 77 (15). Found: C, 59.92; H, 4.85; N, 3.88; S, 8.99. $C_{18}H_{17}NO_5S$ (359.1) req.: C, 60.15; H, 4.77; N, 3.90; S 8.90.

4.8. (4*R*,5*S*)-5-Hydroxymethyl-4-(4-methylthiophenyl)-2-oxazolidinone 10

A mixture of carbamate **9** (0.225 g, 0.64 mmol) in methanol (23 ml), water (1.5 ml), and potassium carbonate (0.29 g, 3 mmol) was stirred at room temperature for 1 h under an argon atmosphere. Methanol was removed under reduced pressure and the aqueous residue extracted with ethyl acetate. The organic solution was washed with water, 20% ammonium chloride, dried, and the solvent evaporated to give TLC pure **10** as a solid (0.13 g, 88 %). Recrystallization from methanol afforded enantiomerically pure[24] **10**. Mp 175.5–176.5 °C, $[\alpha]_D = +31.9$ (*c* 0.9, methanol). IR (KBr) cm^{-1}: 3449–2646 (br), 1747, 1720. ^1H NMR (DMSO-d_6): δ 2.49 (s, 3H, SCH_3), 3.54 (dd, $J = 4.7$, 12.4 Hz, 1H, C*H*HO), 3.63 (dd, $J = 3.8$, 12.4 Hz, 1H, CH*H*O), 4.15 (td, *J*=4.1, 6.3 Hz, 1H, H-5), 4.64 (d, $J = 6.3$ Hz, 1H, H-4), 5.24 (t, $J = 5.8$ Hz, 1H, disappears on treatment with D_2O, CH_2OH), 7.29 (s, 4H, Ar–H). ^1H NMR (CD_3OD): δ 2.47 (s, 3H, SCH_3), 3.69 (dd, $J =$ ca. 4, 12.6 Hz, 1H, C*H*HO), 3.81 (dd, $J = 3.6$, 12.6 Hz, 1H, CH*H*O), 4.32 (ddd, $J = 3.6$, ca. 4, 6.6 Hz, 1H, H-5), 4.76 (d, $J = 6.3$ Hz, 1H, H-4), 7.30 (s, 4H, Ar–H). ^{13}C NMR: δ 15.6 (CH_3), 58.6 (CH), 62.6 (CH_2), 86.6, 127.9, 127.94 (CH), 138.5, 140.7 (C), 161.6 (CO). MS *m*/*z* (%): 239 (M^+, 82), 196 (18), 178 (22), 165 (14), 152 (16), 151 (100), 150 (40), 137 (16), 135 (11), 132 (26), 124 (10), 121 (11), 118 (12), 91 (10). Found: C, 55.30; H, 5.61; N, 5.82; S, 13.38. $C_{11}H_{13}NO_3S$ (239.1) req.: C, 55.21; H, 5.48; N, 5.86; S, 13.37.

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References

1. Kakeya, H.; Morishita, M.; Kobinata, K.; Osono, M.; Ishizuka, M.; Osada, H. *J. Antibiot.* **1998**, *51*, 1126.
2. Kakeya, H.; Morishita, M.; Kosino, H.; Morita, T.; Kobayashi, H.; Osada, H. *J. Org. Chem.* **1999**, *64*, 1052.
3. Sakamoto, Y.; Shiraishi, A.; Seonhee, J.; Nakata, T. *Tetrahedron Lett.* **1999**, *40*, 4203.
4. Seki, M.; Mori, K. *Eur. J. Chem.* **1999**, 2965.
5. Park, J. N.; Ko, Y. S.; Koh, H. Y. *Tetrahedron Lett.* **2000**, *41*, 5553.
6. Milicevic, S.; Matovic, R.; Saicic, R. N. *Tetrahedron Lett.* **2004**, *45*, 955.
7. Davies, S. G.; Hughes, D. G.; Nicholson, R. L.; Smith, A. D.; Wright, A. J. *Org. Biol. Chem.* **2004**, *2*, 1549.
8. Tosaki, S.; Tsuji, R.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 2147; Paraskar, A. S.; Sudalai, A. *Tetrahedron* **2006**, *62*, 5756.
9. Hamersak, Z.; Ljubovic, E.; Mercem, M.; Mesic, M.; Sunjic, V. *Synthesis* **2001**, 1989.
10. Kumar, A. R.; Bhaskar, G.; Madhan, A.; Rao, B. V. *Synth. Commun.* **2003**, *33*, 2907.
11. Tokic-Vujosevic, Z.; Petrovic, G.; Rakic, B.; Matovic, R.; Saicic, R. *Synth. Commun.* **2005**, *35*, 435.
12. Madham, A.; Kumar, A. R.; Rao, B. V. *Tetrahedron: Asymmetry* **2001**, *12*, 2009.
13. Swamy, N. R.; Krishnaiah, P.; Reddy, N.; Venkateswarlu, Y. *J. Carbohydr. Chem.* **2004**, *23*, 217.
14. Sugiyama, S.; Arai, S.; Ishii, K. *Tetrahedron: Asymmetry* **2004**, *15*, 3149.
15. Lin, X.; Bentley, P. A.; Xie, H. *Tetrahedron Lett.* **2005**, *46*, 7849.
16. Matsunaga, S.; Yoshida, T.; Morimoto, H.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8777.
17. Kim, J. D.; Kim, I. S.; Jin, C. H.; Zee, O. P.; Jung, Y. H. *Org. Lett.* **2005**, *7*, 4025.
18. Carda, M.; Gonzales, F.; Sanchez, R.; Marco, J. A. *Tetrahedron: Asymmetry* **2002**, *13*, 1005.
19. Carter, P. H.; LaPorte, J. R.; Scherle, P. A.; Decicco, C. P. *Bioorg. Med. Lett.* **2003**, 1237.
20. Miyata, O.; Asai, H.; Naito, T. *Synlett* **1999**, 1915.
21. Miyata, O.; Koizumi, T.; Asai, H.; Iba, R.; Naito, T. *Tetrahedron* **2004**, *60*, 3893.
22. Miyata, O.; Hashimoto, J.; Iba, R.; Naito, T. *Tetrahedron Lett.* **2005**, *46*, 4015.
23. Castedo, L.; Castro, J. L.; Riguera, R. *Tetrahedron Lett.* **1984**, *25*, 1205.
24. Diastereo- and enantiomeric purity of all compounds synthesized was estimated by HPLC using a Chiralcel-OD-H column.
25. Hamersak, Z.; Sepac, D.; Ziher, D.; Sunjic, V. *Synthesis* **2003**, 375.
26. Boruwa, J.; Borah, J. C.; Kalita, B.; Barua, N. C. *Tetrahedron Lett.* **2004**, *45*, 7355.
27. Fujii, N.; Nakai, K.; Habashita, H.; Hotta, Y.; Tamamura, H.; Otaka, A.; Ibuka, T. *Chem. Pharm. Bull.* **1994**, *42*, 2241.