SYNTHESIS OF THE BYCROFT-GOWLAND STRUCTURE OF MICROCOCCIN P1

Marco A. Ciufolini* and Yong-Chun Shen

Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251, USA, and

Laboratoire de Synthèse et Méthodologie Organiques, Université Claude Bernard Lyon 1 et Ecole Supérieure de Chimie, Physique, Electronique de Lyon, 43, Bd du 11 Novembre 1918, 69622 Villeurbanne cedex, France

Supporting Information

Experimental Procedures and
Spectral data for
Selected Compounds

Acid 8: A solution of **7** (1.2 g, 4.6 mmol), BOC_2O (1.1 g, 5.0 mmol), Et_3N (0.7 mL, 5.1 mmol) and DMAP (28 mg, 0.2 mmol) in 20 mL of CH_2Cl_2 was stirred at rt for 15 min, then it was concentrated to a small volume and eluted through a plug of silica gel (40% EtOAc / hexanes) to give 1.6 g (4.6 mmol, 99%) of the oxazolone N-BOC derivative, pale yellow crystals, m.p. 121.5-123.0°C, R_f = 0.47 (50% EtOAc/hexanes), $[\alpha]_D^{25}$ = –73° (c 6.5). A solution of this intermediate (1.6 g, 4.6 mmol) and $LiOH•H_2O$ (1.1 g, 26.2 mmol) in 52 mL of 50% aqueous THF was stirred at rt for 12 h. The aqueous layer was extracted with hexanes (2 x 20 mL), then it was cooled to 0°C, covered with 30 mL of EtOAc, and carefully acidified to pH 2-3 with 0.5 N aqueous $NaHSO_4$. The organic layer was washed (H_2O, brine), dried (Na_2SO_4) and concentrated to furnish 1.37 g (4.5 mmol, 99%) of **8** as a pale yellow gel. R_f = 0.06 (80% EtOAc / hexanes), $[\alpha]_D^{25}$ (c 2.75) = – 63°. ^1H: 8.19 (s, 1H), 7.27 (br. s, 1H), 6.01 (br. d, 1H, J=9.1), 4.94 (dd, 1H, J_1=9.0, J_2=1.8), 4.64 (dq, 1H, J_1=6.6, J_2=1.9), 2.11 (s, 1H), 1.45 (s, 9H), 1.29 (d, 3H, J=6.4). ^{13}C: 173.1, 163.6, 156.0, 146.0, 128.9, 80.3, 68.4, 57.3, 28.1, 19.0. IR: 3369, 1705, 1504. MS: 302 (M^+), 202 (M^+ – 100), 183, 57 (100%). HRMS: calc for $C_7H_{10}O_3N_2S$ (M^+ – BOC): 202.0412, obs: 202.0416.

Thiazole 10: Ethyl chloroformate (3.0 mL, 1.1 eq) was added to a cold (0°C) solution of N-BOC-D-valine (6.0 g, 27 mmol) and Et_3N (4.6 mL, 1.2 eq) in CH_2Cl_2 (100 mL), then the mixture was warmed to rt during 10 min. Conc. NH_4OH solution was added (5 mL) and after 10 min the mixture was extracted with CH_2Cl_2 (2 x 40 mL). The combined extracts were washed (H_2O),dried (Na_2SO_4) and concentrated to afford 5.6 g (26 mmol, 94%) of white N-BOC D-valine amide, m.p. 161.0 - 162.5°C, $[\alpha]_D^{25}$ = + 2.5° (c 1.05). ^1H: 6.32 (br. s, 1H), 5.92 (br. s, 1H), 5.27 (br. d, 1H, J=8.5), 3.97 (app. t, 1H, J=7.9), 2.10 (octet, 1H, J=6.5), 1.43 (s, 9H), 0.98 (d, 3H, J=6.8), 0.93 (d, 3H, J=6.8). ^{13}C NMR: 174.6, 156.0, 79.7, 59.4, 30.8, 28.3, 19.2, 17.8. IR: 3376, 3341, 1691, 1656. MS : 216 (M^+), 172, 116, 57 (100%). HRMS: calc for $C_{10}H_{20}N_2O_3$: 216.1474, obs: 216.1477. A suspension of this substance and Lawesson's reagent (5.2 g, 13 mmol) in benzene (100 mL) was refluxed for 1h. The mixture was diluted with EtOAc (100 mL), washed (H_2O) dried (Na_2SO_4) and concentrated. A cold (0°C) solution of the crude residue in 60 mL of DME containing solid $KHCO_3$ (5.2 g, 52 mmol) was treated with ethyl bromopyruvate (1.1 eq.). Upon completion of the reaction, the mixture was warmed up to RT and diluted with H_2O (60 mL) and EtOAc (60 mL). The organic phase was washed (H_2O), dried (Na_2SO_4) and concentrated. The residue was redissolved in 30 mL of pyridine and chilled to 0°C. After addition of TFAA (4.4 mL, 31 mmol), the mixture was stirred at 0°C for 1h and then it was concentrated. The residue was dissolved in EtOAc (100 mL), washed (aq. $NaHCO_3$, then H_2O),

dried (Na_2SO_4) and filtered through a plug of silica gel (30% EtOAc / hexanes) to furnish 6.1 g (19 mmol, 72% from N-BOC valine amide) of the N-BOC derivative of **10**, white crystals, m.p. 111.0-112.0°C, R_f = 0.65 (30% EtOAc / hexanes), $[\alpha]_D^{25}$ = +43° (c 0.75, MeOH). ^{1}H: 8.07 (s, 1H), 5.31 (br. d, 1H, J=8.3), 4.90 (dd, 1H, J_1=9.0, J_2=5.8), 4.42 (q, 2H, J=7.1), 2.45 (septet, 1H, J=6.5), 1.45 (s, 9H), 1.40 (t, 3H, J=7.1), 0.98 (d, 3H, J=6.8), 0.90 (d, 3H, J=6.8). ^{13}C: 127.8, 160.6, 154.8, 146.5, 126.4, 79.0, 60.5, 57.4, 32.5, 27.6, 18.7, 16.6, 13.7. IR: 3150, 1722, 1503. MS : 328 (M^+), 185 (100%). HRMS: calc for $C_{15}H_{24}N_2O_4S$: 328.1457, obs: 328.1457. A solution of this intermediate in CH_2Cl_2 (20 mL) and TFA (10 mL) was stirred at rt for 10 min, then it was concentrated. A solution of the residue in EtOAc (50 mL) was washed ($NaHCO_3$, H_2O), dried (Na_2SO_4) and concentrated to afford 4.3 g (19 mmol, 100%) of **10** as a pale gel. Optical integrity of was verified ^{1}H NMR analysis of the crude Mosher amide (MTPA, DCC). R_f = 0.34 (80% EtOAc / hexanes), $[\alpha]_D^{25}$ = + 30° (c 0.50). ^{1}H: 8.12 (s 1H), 4.42 (q, 2H, J=7.1), 4.21 (br. d, 1H, J=4.8), 2.30 (sextet, 1H, J=6.5), 1.40 (t, 2H, J=7.1). ^{13}C: 184.4, 161.4, 146.6, 127.2, 61.2, 58.9, 34.0, 191.1, 16.9, 14.2. IR: 3577, 1725. MS: 228 (M^+), 198, 185 (100%, M^+–43). HRMS: calc for $C_{10}H_{16}N_2O_2S$: 228.0928, obs: 228.0932.

Dipeptide 11: A mixture of acid **8** (0.7 g, 2.3 mmol), amine **10** (0.5 g, 2.3 mmol) and DCC (0.6 g, 2.7 mmol) in CH_2Cl_2 (20 mL) was stirred at RT for 30 min, then it was treated with 20 mL of sat. aq. $NaHCO_3$. The organic layer was washed ($NaHCO_3$, H_2O, brine), dried (Na_2SO_4) and passed through a plug of silica gel (40% EtOAc/hexanes) to collect 1.07 g (2.1 mmol, 91%) of **11**. R_f = 0.68 (80% EtOAc / hexanes), $[\alpha]_D^{25}$ = –48° (c 0.40). ^{1}H: 8.09 (s, 1H), 8.07 (s, 1H), 7.93 (br. d, 1H, J=9.3), 5.67 (br. d, 1H, J=9.2), 5.31 (dd, 1H, J_1=9.1, J_2=7.1), 4.92 (br. d, 1H, J=9.0), 4.61 (app. q, 1H, J=5.2), 4.42 (q, 2H, J=7.1), 2.59 (m, 1H, J=6.7), 1.48 (s, 9H), 1.40 (t, 3H, J=7.1), 1.35 (d, 3H, J= 6.4), 1.04 (d, 3H, J=6.8), 0.99 (d, 3H, J=6.7). ^{13}C: 173.1, 171.1, 160.6, 160.5, 155.4, 148.4, 146.6, 126.7, 123.7, 79.4, 68.2, 60.8, 57.8, 56.0, 32.4, 27.7, 19.4, 19.1, 17.6, 13.8. IR: 3409, 1709, 1530. MS: 512 (M^+), 498, 469 (100%), 440, 412, 397, 369, 340. HRMS: calc for $C_{22}H_{32}N_4O_6S_2$: 512.1763, obs: 512.1760.

Dipeptide 12: A solution of **11** (1.1 g, 2.1 mmol) in CH_2Cl_2 (10 mL) and TFA (5 mL) was stirred at rt for 10 min, then it was concentrated. A solution of the residue in CH_2Cl_2 (30 mL) was washed (sat. aq. $NaHCO_3$, H_2O), dried (Na_2SO_4) and concentrated to obtain 0.9 g (2.1 mmol, 100%) of **12**. R_f = 0.05 (50% EtOAc / hexanes), $[\alpha]_D^{25}$ = –31° (c 1.0). ^{1}H: 8.08 (s, 1H), 8.07 (s. 1H), 7.95 (br. d, 1H, J=9.1), 5.31 (dd, 1H, J_1=9.3, J_2=7.2), 4.41 (q, 2H, J=7.1), 4.20 (dq, 1H, J_1=6.4, J_2=4.9), 4.03 (d, 1H, J=4.9), 2.62 (sextet, 1H, J=6.8), 1.39 (t, 3H, J=7.1), 1.27

(d, 3H, J=6.3), 1.03 (d, 3H, J= 6.8), 0.98 (d, 3H, J= 6.7). ^{13}C: 175.4, 171.2, 160.7, 160.5, 148.4, 146.4, 146.8, 126.8, 123.9, 69.7, 90.9, 59.1, 56.0, 32.6, 19.3, 19.2, 17.7, 13.9. IR: 3396, 1729, 1662, 1530. MS: 412 (M^+), 368 (100%). HRMS calc for $C_{17}H_{24}N_4O_4S_2$: 412.1239, obs: 412.1244.

Tripeptide 13: A mixture of **5** (0.5 g, 1.8 mmol), amine **12** (0.8 g, 1.8 mmol) and DCC (0.4 g, 2.1 mmol) in CH_2Cl_2 (15 mL) was stirred at rt for 30 min, then it was filtered (removal of precipitate), diluted with more CH_2Cl_2, washed ($NaHCO_3$, H_2O, brine), dried (Na_2SO_4) and concentrated to give 1.2 g (1.8 mmol, 97 %) of **13** as a white foam. R_f = 0.68 (100% EtOAc), $[\alpha]_D^{25}$ = –58° (c 1.1). ^{1}H: 8.08 (s, 2H), 7.92 (br. d, 1H, J=9.0), 7.13 (br. d, 1H, J=8.0), 5.32 (dd, 1H, J_1=9.1, J_2=7.1), 5.25 (br. d, 1H, J=8.9), 4.55 (m, 1H), 4.42 (q, 2H, J=7.1), 4.32 (m, 1H), 3.94 (d, 1H, J=7.3), 2.59 (m, 1H), 1.62 (d, 6H, J= 6.2), 1.42 (d, 3H, J=6.3), 1.41 (t, 3H, J=7.1), 1.40 (s, 9H), 1.31 (d, 3H, J=6.4), 1.03 (d, 3H, J=6.8), 0.99 (d, 3H, J=6.7). ^{13}C: 171.1, 171.0, 170.0, 160.9, 160.4, 151.8, 148.6, 146.8, 126.9, 124.1, 94.5, 80.6, 77.2, 73.8, 48.7, 67.0, 61.1, 56.3, 32.8, 28.0, 27.1, 24.9, 19.4, 19.3, 18.8, 17.8, 14.0. IR: 3369, 1669, 1536. MS: 653 (M^+), 538 (100%). HRMS: calc for $C_{29}H_{43}N_5O_8S_2$: 653.2553, obs: 653.2558.

Amine 3: Mesyl chloride (0.2 mL, 2.1 mmol) was added to a cold (0 °C) solution of **13** (1.2 g, 1.8 mmol) and Et_3N (0.3 mL, 2.1 mmol) in CH_2Cl_2 (15 mL). After 10 min, the organic phase was washed (sat. aq. $NaHCO_3$, H_2O, brine), dried (Na_2SO_4) and concentrated to afford 1.3 g of mesylate ester, a solution of which (0.6 g, 0.8 mmol) in CH_2Cl_2 (5 mL) and TFA (5 mL) was kept at rt for 10 min, then it was concentrated. A solution of the residue in THF (5 mL) and 0.2 N HCl (5 mL) was stirred for 30 min, then it was diluted with $CHCl_3$ (25 mL), washed (sat. aq. $NaHCO_3$, H_2O), dried (Na_2SO_4) and concentrated. A solution of the residue and DBU (130.0 μL, 0.8 mmol) in $CHCl_3$ (10 mL) was stirred at rt for 0.5 h, then it was directly applied to a plug of silica gel and eluted (5% MeOH / $CHCl_3$) to furnish 0.4 g (0.7 mmol, 88%) of **3**, pale oil. R_f = 0.19 (5% MeOH/$CHCl_3$), $[\alpha]_D^{25}$ = – 20° (c 2.6). ^{1}H: 9.23 (br. s, 1H), 8.53 (br. d, 1H, J=9.8), 8.05 (s, 1H), 7.93 (s, 1H), 6.43 (q, 1H, J= 7.1), 5.32 (dd, 1H, J_1=9.7, J_2=7.5), 4.55 (dq, 1H, J_1=6.4, J_2=2.5), 4.40 (q, 2H, J=7.1), 3.59 (br. s, 1H), 2.42 (sextet, 1H, J= 6.9), 1.89 (d, 1H, J= 7.1), 1.39 (t, 3H, J= 7.1), 1.35 (d, 3H, J= 6.2), 1.05 (d, 3H, J= 6.8), 0.94 (d, 3H, J= 6.7). ^{13}C: 172.9, 170.7, 166.4, 161.1, 160.4, 148.7, 146.9, 129.1, 126.9, 126.7, 123.0, 68.0, 61.4, 59.7, 55.8, 33.9, 19.4, 19.2, 18.4, 14.4, 14.2. IR: 3396, 3303, 1716, 1663, 1530. MS: 495 (M^+), 451, 421, 394 (100%). HRMS: calc for $C_{21}H_{29}O_5N_5S_2$: 495.1610, obs: 495.1610.

Compound 17: A mixture of **14** (11 mg, 15 μmol) and $LiOH•H_2O$ (1.3 mg, 30 μmol) in 1 mL of 50% aq. THF was stirred at rt for 45 min, then it was cooled to 0 °C and acidified to pH 2 with 0.5 N aq. $NaHSO_4$. Extraction with EtOAc (5 mL), drying (Na_2SO_4), and concentration afforded crude **15**, which was dissolved in CH_2Cl_2 (1 mL) and treated with Et_3N (6.2 μL, 44 μmol), BOC_2O (6.5 mg, 30 μmol) and DMAP (0.1 mg, 0.7 μmol, added as a CH_2Cl_2 solution). After 10 min, the reaction was quenched with 0.2 mL of H_2O. The cold (0°C) mixture was acidified to pH 2 with 0.5 N aq. $NaHSO_4$ and extracted with EtOAc (5 mL). The organic phase was dried (Na_2SO_4) and concentrated to afford **16**. A solution of this crude material, amine salt **6** (7.6 mg, 30 μmol) and Et_3N (8.4 μL, 60 μmol) in CH_3CN (0.2 mL) was stirred at rt during addition of BOP-Cl (7.6 mg, 30 μmol). After 30 min, sat. aq. $NaHCO_3$ (5 mL) and ether (5 mL) were added of Et_2O. The organic phase was dried (Na_2SO_4) and concentrated to furnish 13 mg (13 μmol, 84%) of **17**, m.p. 112.0-114.0°C. R_f = 0.12 (60% EtOAc / hexanes), $[\alpha]_D^{25}$ (c 0.65, $CHCl_3$) = – 21°. ^{1}H NMR: 8.35 (d, 1H, J=8.2 Hz), 8.24 (s, 1H), 8.24 (d, 1H, J=8.1 Hz), 8.19 (s, 1H), 8.02 (s, 1H), 7.32 (t, 1H, J=1.2 Hz), 7.08 (br. t, 1H, J=6.2 Hz), 6.88 (br. s, 1H), 5.50 (br. d, 1H, J=7.8 Hz), 5.04 (d, 1H, J=4.0), 5.02 (m, 1H), 4.90 (d, 2H, J=1.1), 4.52 (m, 1H), 4.37 (dq; 1H; J_1=6.5, J_2=2.1), 3.41 (m, 2H), 2.05 & 2.04 (s, 3H total), 1.48 (d, 3H, J=7.0), 1.46 (s, 9H), 1.22 & 1.18 (d, 6H total, J=6.5 Hz), 0.96 (s, 9H), 0.14 (s, 6H). ^{13}C NMR: 171.3, 168.8, 166.8, 162.1, 157.7, 157.1, 154.3, 153.5, 150.3, 149.8, 149.2, 148.9, 146.9, 145.1, 140.0, 130.0, 127.6, 124.4, 121.7, 120.2, 118.8, 116.0, 84.9, 83.3, 75.6, 69.4, 66.3, 62.3, 62.2, 56.7, 43.7, 27.9, 25.9, 20.2, 18.3, 17.5, -5.3, -5.4. IR: 3372, 3300, 1841, 1736, 1645. MS (FAB): 1021 (M^++Na, 100%), 999 (M^++1).

Aldehyde 19: A solution of **17** (12 mg, 12 μmol) and TBAF (100 μmol) in THF (0.5 mL) was stirred at rt for 30 min, then it was diluted with EtOAc (5 mL). The organic phase was washed (H_2O, brine), dried (Na_2SO_4) and concentrated. The residue and activated MnO_2 (5.2 mg, 60 μmol) in EtOAc (2 mL) was stirred at rt for 1h. The mixture was filtered and concentrated and the crude aldehyde in CH_2Cl_2 (2 mL) was treated with Et_3N (4.2 μl, 30 μmol) and MsCl (2.0 μl, 24 μmol) at 0 °C for 10 min. The mixture was diluted with sat. aq. $NaHCO_3$ (5 mL) and EtOAc (5 mL. The organic phase was washed (aq. $NaHCO_3$, H_2O), dried (Na_2SO_4) and concentrated. A solution of crude mesylate **18** and DBU (3.6 μl, 24 μmol) in 1 mL of $CHCl_3$ was stirred at RT for 0.5 h, then it was filtered through a plug of silica gel with EtOAc to give 7.1 mg (8.2 μmol, 68%) of **19** as a pale gel. R_f = 0.42 (100% EtOAc), $[\alpha]_D^{25}$ = + 14° (c 0.41). ^{1}H: 10.06 (s, 1H), 8.72 (s, 1H), 8.38 (d, 1H, J=8.1), 8.38 (s, 1H), 8.26 (s, 1H), 8.24 (s, 1H), 8.23 (s, 1H), 8.19 (d, 1H, J=8.2), 6.63 (q, 1 H, J=7.1), 6.53 (br. s, 1H), 5.04 (m, 1H), 4.94 (d, 1H, J=3.9), 4.45

(m, 1H), 3.52 (m, 2H), 2.03 (s, 3H), 1.87 (d, 3H, J=7.1), 1.46 (d, 3H, J=7.0), 1.46 (s, 9H), 1.28 & 1.26 (d, 3H total, J=6.4). IR: 3371, 1808, 1723, 1690, 1658. MS (FAB): 887 (M^++Na), 788 (M^+ – 100), 173 (100%).

Compound 20: A mixture of aldehyde **19** (6.0 mg, 6.9 μmol), $NaClO_2$ (1.6 mg, 14 μmol), NaH_2PO_4 (1.8 mg) and a drop of 2-methyl-2-butene in 50% aq. THF (1.0 mL) was stirred at rt for 2 h, then it was acidified (pH 2) with 0.5 N aq. $NaHSO_4$ and extracted with EtOAc. The extracts were dried (Na_2SO_4) and concentrated. Crude **4** thus obtained and tripeptide **3** (4.1 mg, 8.3 μmol) in CH_3CN (0.2 mL) was treated with Et_3N (1.9 μl, 14 μmol), and BOP-Cl (3.5 mg, 14 μmol) at rt for 30 min. The mixture was diluted with sat. aq. $NaHCO_3$ (2 mL) and EtOAc (3 mL). The organic phase was washed (aq. $NaHCO_3$, H_2O), dried (Na_2SO_4) and concentrated to afford 7.1 mg (5.2 μmol, 76%) of **20**. R_f = 0.32 (5% MeOH / $CHCl_3$), $[\alpha]_D^{25}$ = +53° (c 0.35). ^{1}H: 9.01 (br. s, 1H), 8.75 (br. s, 1H), 8.67 (br. d, 1H, J=9.4), 8.38 (d, 1H, J=8.1), 8.30 (s, 1H), 8.30 (d, 1H, J= 8.1), 8.25 (s, 1H), 8.23 (s, 1H), 8.08 (s, 1H), 8.08 (s, 1H), 7.95 (s, 1H), 6.63 (q, 1 H, J=7.1), 6.52 (br. s, 1H), 6.40 (br. m, 1H), 6.40 (q, 1H, J=7.1), 5.34 (dd; 1H; J_1=9.5, J_2=7.4), 5.00 (d, 1H, J=3.9), 4.99 (m, 1H), 4.72 (m, 1H), 4.48 (q, 2H, J=7.1), 4.53-4.35 (m, 2H), 3.50 (m, 2H), 2.37 (m, 1H), 2.03 (s, 3H), 1.88 (br. d, 6H, J=7.0), 1.48 (d, 3H, J=7.0), 1.47 (s, 9H), 1.42 (d, 3H, J=6.4), 1.40 (t, 3H, J=7.1), 1.27 (d, 3H, J=6.5), 1.03-0.90 (m, 6H total). IR: 3365, 1749. MS (FAB): 1380 (M^++Na), 55 (100%).

Bycroft-Gowland "Micrococcin P1," 2a: A mixture of **20** (5.0 mg, 3.7 μmol) and $LiOH•H_2O$ (1.5 mg, 36 μmol) in 0.5 mL of THF and 0.5 mL of H_2O was stirred at RT for 12 h, then it was acidified (pH 2-3) with 0.5 M aqueous $NaHSO_4$ and extracted with EtOAc. The organic phase was dried (Na_2SO_4) and concentrated. The crude acid was dissolved in dioxane (0.5 mL) and carefully treated with a saturated dioxane solution of anhydrous HCl at 0 °C for 25 min. After removal of volatiles the crude residue in 0.4 mL of DMF was treated with DPPA (0.8 μl, 3.7 μmol) and Et_3N (1.5 μl, 11 μmol) at 0 °C for 36 h. The solution was diluted with 5 mL of H_2O and 5 mL of EtOAc. The organic phase was washed (dilute aq. $NaHSO_4$, dilute aq. $NaHCO_3$), dried (Na_2SO_4) and directly applied to a preparative TLC plate. Elution with 10% MeOH / $CHCl_3$ furnished 2.7 mg (2.4 μmol, 65%) of **2a** as a yellow powder. R_f = 0.48 (10% MeOH / $CHCl_3$), $[\alpha]_D^{25}$ = + 24° (c 0.13). ^{1}H: 8.89 (br. d, 1H, J=10.0), 8.75 (br. s, 1H), 8.51 (br. s, 1H), 8.41 (d, 1H, J=8.1), 8.27 (s, 1H), 8.23 (s, 1H), 8.23 (br. d, 1H, J=9.9), 8.14 (d, 1H, J=8.1), 8.12 (s, 1H), 8.00 (s, 1H), 7.97 (br. d, 1H, J= 10.0), 7.92 (s, 1H), 7.91 (s, 1H), 6.65 (q, 1 H, J=6.7), 6.55 (br. t, 1H, J=5.7), 6.48 (q, 1H, J=6.7), 5.33 (br. s, 1H), 5.22 (app t,

1H, J=9.4), 4.83 (m, 1H), 4.82 (d, 1H, J=7.1), 4.70 (d, 1H, J=6.4), 4.14-3.98 (m, 2H), 3.65 (br. s, 1H), 3.60 (m, 1H), 3.15 (m, 1H), 2.83 (br. s, 1H), 2.43 (m, 1H), 1.88 (br. d, 6H, J=7.1), 1.40 (d, 3H, J=6.6), 1.36 (d, 3H, J=6.5), 1.34 (d, 3H, J=6.5), 1.22 (d, 3H, J=6.6), 0.73 (d, 3H, J=6.6). IR:3385, 1730, 1658. MS (FAB): 1166 (M^++Na), 1144 (M^++H), 69 (100%). HRMS (FAB): calc for $C_{48}H_{49}S_6N_{13}O_9Na$ (M^++Na): 1166.200, obs: 1166.202.