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The stereoselective total synthesis of xestodecalactone C and *epi*-sporostatin via the Prins cyclisation

J. S. Yadav *, N. Thrimurtulu, K. Uma Gayathri, B. V. Subba Reddy, A. R. Prasad

Pheromone Group, Organic Division I, Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh 500 007, India

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ABSTRACT

Syntheses of xestodecalactone C and *epi*-sporostatin are described utilising Prins cyclisations, Mitsunobu reaction and intramolecular Friedel–Crafts acylation. The approach is convergent and highly stereoselective.

Marine microorganisms are a source for novel bioactive molecules. More than 800 microorganisms have so far been isolated from marine sediments and organisms.[1,2] Xestodecalactones A, B and C (**II, IIIa** and **IIIb**) were isolated from the fungus *Penicillium cf. montanense*, which in turn was isolated from *Xestospongia exigua*. These molecules are structurally related to a number of compounds isolated from terrestrial fungi, including sporostatin (**I**) and curvularins (**IV, Va and Vb**) (Fig. 1).

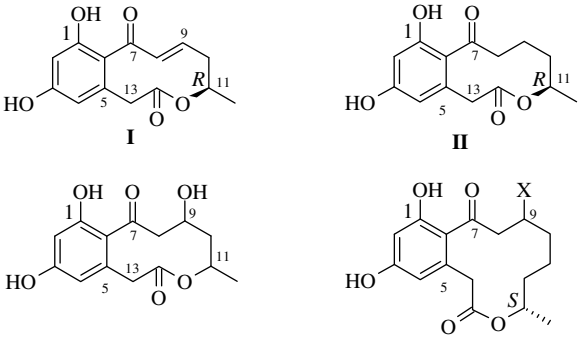

Figure 1. Sporostatin (**I**), xestodecalactone A (**II**), xestodecalactone B, C (**IIIa, IIIb**) and curvularins (**IV, Va and Vb**).

Sporostatin (M5032, **I**) isolated from the fungus *Sporormiella* sp., is an inhibitor of cyclic adenosine 3′,5′-monophosphate phosphodiesterase.[1] All these compounds contain a 10-membered macrolide with 1,3-dihydroxybenzene ring. Xestodecalactones A–C have been found to exhibit antibacterial and antifungal activities.[2] They are also found to be a specific inhibitor of epidermal growth factor (EGF) receptor, tyrosine kinase in vitro. In view of their biological activity, we were interested in the total synthesis of xestodecalactone C and sporostatin by means of Prins cyclisation.

The Prins cyclisation is a powerful synthetic tool for the construction of multi-substituted tetrahydropyran systems and has been utilised in the synthesis of several natural products.[3] Our group has made a significant effort to explore the utility of Prins cyclisation in the synthesis of various polyketide intermediates and applied it to the total synthesis of some natural products.[4] As a part of our ongoing programme on the total synthesis of natural products, we herein report the synthesis of xestodecalactone C and *epi*-sporostatin.

In our retrosynthetic analysis (Scheme 1), we envisaged that the target molecules (**IIIb** and **I**) could be achieved from a common intermediate **12**, which was viewed as being obtained from a Mitsunobu reaction and intramolecular Friedel–Crafts acylation. It was proposed to obtain the 1,3-diol **8** from 2,4,6-trisubstituted tetrahydropyran **4**, which in turn would be obtained via the Prins cyclisation of homoallylic alcohol **3** and acetaldehyde.

Accordingly, the synthesis of xestodecalactone (**IIIb**) and *epi*-sporostatin (**I**) began with chiral homoallyl alcohol (**3**). The precursor **3** was prepared in two steps by Cu(I)-mediated regioselective

* Corresponding author. Tel.: +91 40 27193030; fax: +91 40 27160512.
E-mail address: yadavpub@iict.res.in (J. S. Yadav).

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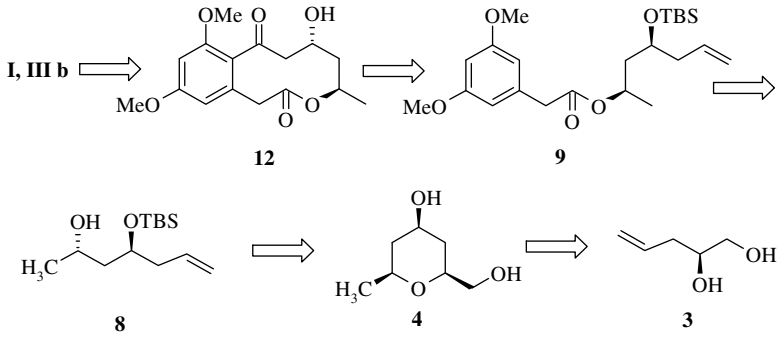
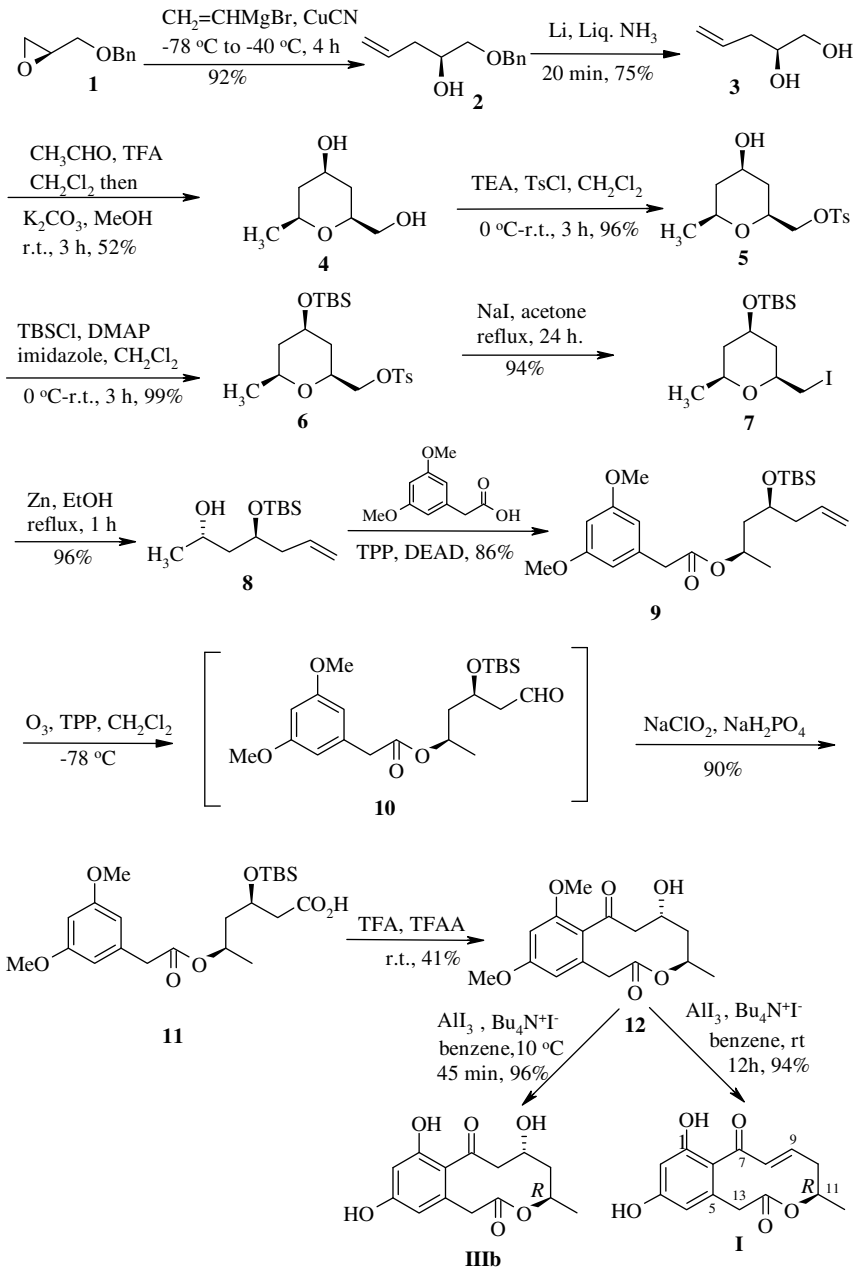


Scheme 1. Retrosynthetic analysis of xestodecalactone C and *epi*-sporostatin.

opening[5] of *S*-(−)-benzyl glycidyl ether with vinylmagnesium bromide and by subsequent reductive cleavage of the benzyl ether with Li or Na in liquid ammonia. Prins cyclisation of **3** with acetaldehyde in the presence of TFA (10 equiv), followed by hydrolysis of the resulting trifluoroacetate, gave trisubstituted pyran **4** in 52% yield.[6] The stereochemistry of **4** was assumed to be in anticipated



Scheme 2. Synthetic sequence of **IIIb** and **I**.

line with previous results.[4–6] However, it was later proved after elaborating compound **4** to the target molecule which in all respects was identical with the reported one. The chemoselective tosylation of primary alcohol in compound **4** with 1.1 equiv of tosyl chloride in the presence of TEA in DCM gave the corresponding tosylate **5** in 96% yield.[7,12] TBS protection of the secondary alcohol **5** with TBSCl, DMAP and imidazole provided the corresponding TBS ether **6** in 91% yield. Treatment of tosylate **6** with NaI in refluxing acetone gave the respective iodo compound **7** in 94% yield, which on exposure to activated Zn in refluxing ethanol furnished key intermediate **8** with the required anti-1,3-diol system in 96% yield. Alcohol **8** when subjected to standard Mitsunobu reaction conditions using DEAD, PPh_3 and 3,5-dimethoxyphenylacetic acid in THF gave compound **9** in 86% yield.[8] Ozonolysis of the olefin **9** followed by further oxidation with $NaClO_2$ and NaH_2PO_4 gave the corresponding acid **11** in 90% yield. The desired macrolide **12** was obtained in 41% yield (at 25 °C, 8 h) by intramolecular Friedel–Crafts reaction of the carboxylic acid **11** with a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride.[9] Demethylation of **12** using freshly prepared AlI_3 at 10 °C for 45 min gave the target molecule **IIIb**[9e–g] in 96% yield, whereas the same reaction at room temperature over 12 h furnished **I** in 94% yield.[9a,9d]

The formation of **IIIb** and **I** in a single step from **12** under different reaction conditions maybe attributed to the versatility of aluminium iodide. Deprotection of the methoxy groups of **12** occurred using the freshly prepared AlI_3. Upon prolonged reaction conditions, aluminium iodide, due to its acidic property, has been observed to catalyse the dehydration of the free OH present in **12**, along with the expected demethylation thereby resulting in the formation of **I**. The target molecule **IIIb** was identical in all respects to the natural product (Scheme 2).[10]

The spectral data and melting point of **I** were identical with those of the natural product.[11] The specific rotation of our synthetic *epi*-sporostatin **I** was +18.8°, which is exactly the opposite optical rotation to that reported by Yaginuma and co-workers,[11] thereby confirming stereochemistry of the chiral centre at C11 carbon as '*R*'. The specific rotation of naturally occurring sporostatin was −18.8° for which the configuration at C11 carbon centre was reported as (*S*). Therefore, the product **I** formed from **12** is the unnatural *epi*-sporostatin with 'R' configuration.

In conclusion, we have proved the versatility of the Prins cyclisation in natural product synthesis by achieving the stereoselective synthesis of xestodecalactone (**IIIb**) and sporostatin (**I**), by employing a 10-step sequence. Further applications of the Prins cyclisation in the synthesis of natural products are in progress, and will be disclosed in due course.

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12. *Experimental procedure*: *(2S,4R,6S)-4-hydroxy-6-methyl-6-methyltetrahydro-2H-2-pyranyl)methyl-4-methyl-1-benzenesulfonate* (**5**): To a solution of diol **4** (2.0 g, 13.68 mmol) in dry CH_2Cl_2 (15.0 mL), triethylamine (3.81 mL, 27.36 mmol) was added at 0 °C. Then tosyl chloride (2.86 g, 15.04 mmol) was added over 2 h. The resulting mixture was allowed to warm to room temperature, and stirred for 3 h. Then the reaction mixture was treated with aqueous 1 N HCl (10 mL), and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed with saturated $NaHCO_3$ (15 mL) and water (15 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography of the crude product afforded tosylate **5** (3.94 g, 96%) as a gummy liquid. R_f = 0.5 (SiO_2, 80% EtOAc in hexane). $[\alpha]_D^{25}$ +34.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.75 (d, 2H, *J* = 8.0 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 4.04–3.87 (m, 2H), 3.82–3.64 (m, 1H), 3.58–3.42 (m, 1H), 3.42–3.28 (m, 1H), 2.45 (s, 3H), 2.13 (m, 1H), 1.90–1.80 (m, 3H), 1.15 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.1, 132, 129, 127, 72.8, 72.12, 67.35, 42.36, 36.54, 21.73; IR (Neat): ν 3410, 2926, 2855, 1741, 1597, 1451, 1358, 1176, 974 cm^{-1}; HRMS calcd for $C_{14}H_{20}O_5NaS$ (M+Na)$^+$ 323.0929. Found: 323.0932. *(2S,4S)-4-(tert-Butyl-dimethyl-silanyloxy)-hept-6-en-2-ol* (**8**): To the iodide **7** (2.2 g, 5.94 mmol) in ethanol (80 mL), commercial zinc dust (5.82 g, 89.10 mmol) was added. The resulting mixture was refluxed for 1 h, and then cooled to 25 °C. Addition of solid ammonium chloride (8.17 g) and ether (120 mL) followed by stirring for 5 min gave a gray suspension. The suspension was filtered through Celite, and filtrate was concentrated in vacuo. Purification by flash chromatography gave **8** (1.39 g, 96%) as a colourless liquid. R_f = 0.4 (SiO_2, 10% EtOAc in hexane). $[\alpha]_D^{25}$ +39.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82–5.60 (m, 1H), 5.12–5.00 (m, 2H), 4.19–3.82 (m, 2H), 2.35–2.21 (m, 2H), 1.59–1.50 (m, 2H), 1.14 (d, 3H, *J* = 6.2 Hz), 0.89 (s, 9H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.0, 117.3, 71.1, 64.3, 43.0, 32.4, 25.7, 18.6, −4.2; IR (Neat): ν 3452, 2942, 1640, 1098, 1034, 916, 702 cm^{-1}; HRMS calcd for $C_{13}H_{28}O_2NaSi$ (M+Na)$^+$, 267.1756. Found: 267.1766. *(1R,3S)-(3,5-Dimethoxy-phenyl)-aceticacid-3-(tert-butyl-dimethyl-silanyloxy)-1-methyl-hex-5-enyl ester* (**9**): To a well-stirred solution of alcohol **8** (0.20 g, 0.81 mmol) and triphenylphosphine (0.32 g, 1.23 mmol) in dry benzene (5 mL) at room temperature was added a solution of 3,5-dimethoxyphenylacetic acid (0.16 g, 0.81 mmol) and DEAD (0.21 g, 1.23 mmol) in benzene (5 mL). The mixture was stirred for 14 h. Solvent was evaporated, and the residue was washed with dry ether and filtered through a sintered funnel. The filtrates were dried over anhydrous Na_2SO_4, and evaporation of the solvent followed by chromatography of the crude residue afforded pure ester **9** (0.29 g, 86% yield) as a pale pink coloured viscous liquid. $[\alpha]_D^{25}$ +4.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.4–6.32 (m, 2H), 6.29 (s 1H), 5.80–5.60 (m, 1H), 5.05–4.09 (m, 2H), 3.79 (s, 6H), 3.68–3.52 (m, 1H), 3.48 (s, 2H), 2.30–2.05 (m, 2H), 1.80–1.50 (m, 2H), 1.20 (d, 3H, *J* = 5.8 Hz), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.2, 160.7, 134.7, 117.0, 107.0, 99.1, 68.7, 55.2, 42.9, 42.0, 41.2, 25.7, 20.3. IR (Neat): ν 3075, 2930, 2856, 1733, 1600, 1465, 1431, 1352, 1293, 1252, 1155, 915 cm^{-1}; HRMS calcd for $C_{23}H_{38}O_5NaSi$ (M+Na)$^+$ 445.2386. Found: 445.2400. *(1R,3S)-3-(tert-Butyl-dimethyl-silanyloxy)-5-[2-(3,5-dimethoxy-phenyl)-acetoxy]-hexenoic acid* (**11**): Ozone was bubbled through a solution of **9** (0.15 g, 0.35 mmol) in CH_2Cl_2 (2 mL) at −78 °C until no unreacted starting material was observed on TLC. The reaction mixture was purged with N_2 to remove the excess of ozone and cooled to 0 °C, Ph_3P (0.18 g, 0.70 mmol) was added, and the mixture was stirred for 2 h. The mixture was concentrated in vacuo. After adding hexane, the mixture was filtered through Celite pad. Then the residue was washed with hexane, and the filtrate was dried over Na_2SO_4, concentrated under reduced pressure and the crude aldehyde **10** was subjected to the next reaction without further purification. To a stirred solution of the crude aldehyde **10** in *t*-BuOH (1 mL) was added methyl-2-butene (0.5 mL) in *t*-BuOH (0.5 mL). The reaction mixture was cooled (0 °C) and treated with a solution of $NaClO_2$ (0.086 g, 0.95 mmol)

and NaH_2PO_4 (0.344 g, 2.87 mmol) in H_2O (1 mL). After 1.5 h, the reaction mixture was diluted with brine (3 mL) and Et_2O (3 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by flash chromatography (Et_2O) to afford the acid **11** (0.12 g, 90%). R_f = 0.25 (SiO_2, 30% EtOAc in hexane). $[\alpha]_D^{25}$ +3.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.47–6.30 (m, 2H), 5.17–4.90 (m, 1H), 4.18–4.01 (m, 1H), 3.76 (s, 6H), 3.50 (s, 2H), 2.46-2.42 (m, 2H), 2.00–1.51 (m, 2H), 1.23 (d, 3H, *J* = 5.8 Hz), 0.85 (s, 9H), 0.03 (s, 6H); ^{13}C NMR ($CDCl_3$,75 MHz): δ 179.0, 172.9, 161.0, 150.5, 146.1, 128.7, 123.3, 107.4, 99.0, 69.3, 55.2, 41.7, 38.3, 19.5, 18.3; IR (Neat): ν 3759, 3678, 3449, 2926, 2855, 1740, 1602, 1463, 1376, 1050, 835 cm^{-1}. HRMS calcd for $C_{22}H_{36}O_7NaSi$ (M^++Na): 463.2128. Found: 463.2116. Xestodecalactone C (**5a**): Iodine (0.29 g, 1.16 mmol) was added to a mixture of aluminium (0.042 g, 1.56 mmol) in dry benzene. The mixture was refluxed for 1 h, and then cooled to room temperature. A mixture of *n*-$Bu_4N^+I^-$ (0.0018 g, 0.0050 mmol) and compound **12** (0.012 g, 0.038 mmol) in dry benzene (8 mL) was added. The resulting mixture was stirred for 45 min at 10 °C and quenched with water. After acidification with 2 N HCl, the mixture was extracted with EtOAc (3 × 10 mL). The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 1:1) to afford the xestodecalactone **IIIb** (0.010 mg, 96%) as a white solid, mp 167–168 °C; $[\alpha]_D^{25}$ +24 (*c* 0.5, CH_3OH); ^{1}H NMR (DMSO, 300 MHz): δ 9.90 (s, 1H), 9.70 (s, 1H), 6.27 (d, 1H, *J* = 1.6 Hz), 6.09 (s, 1H), 4.76 (d, 1H, *J* = 4.0 Hz), 4.72 (dd, 1H, *J* = 11.2, 5.6 Hz), 3.95 (br s, 1H), 3.82 (d, 1H, *J* = 18.8 Hz), 3.48 (d, 1H, *J* = 18.8 Hz), 3.08 (dd, 1H *J* = 14.8, 10.4 Hz), 2.81 (d, 1H, *J* = 14.6 Hz), 1.83 (d, 1H, *J* = 13.0 Hz), 1.64 (dd, 1H, *J* = 14.8, 11.2 Hz), 1.08 (d, 3H, *J* = 6.5 Hz). ^{13}C NMR (DMSO, 75 MHz): δ 204.0, 167.4, 159.1, 157.0, 134.1, 121.8, 110.0, 101.1, 70.6, 67.8, 55.3, 45.9, 20.6. IR (Neat): ν 3343, 2923, 1739, 1650, 1376 cm^{-1}. MS(LCMS): *m*/*z* 303 (M+Na)$^+$. HRMS calcd for $C_{14}H_{16}O_6$: 303.0839. Found: 303.0843. *epi*-sporostatin (**I**): To a suspension of aluminium (0.042 g, 1.56 mmol) in dry benzene was added a solution of iodine (0.29 g, 1.16 mmol) in dichloromethane. The mixture was refluxed for 1 h, cooled to room temperature, and then *n*-$Bu_4N^+I^-$ (0.0018 g, 0.0050 mmol) and **12** (0.012 g, 0.038 mmol) in dry benzene (8 mL) were added. The mixture was stirred for 12 h at room temperature and quenched with water. After acidification with 2 N HCl, the mixture was extracted with EtOAc (3 × 10 mL). The organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc, 2:1) to afford *epi*-sporostatin **I** (0.009 g, 94%) as a white solid, mp 198–200 °C; $[\alpha]_D^{25}$ +18.8 (*c* 0.5, CH_3OH); ^{1}HNMR (DMSO, 300 MHz): δ 13.59 (s, 1H), 10.75 (s, 1H), 6.80 (d, 1H, *J* = 15.8 Hz), 6.32 (s, 1H), 6.22 (s, 1H), 6.01–5.92 (m, 1H), 5.11–5.01 (m, 1H), 4.07 (d, 1H, *J* = 16.8 Hz), 3.92–3.82 (m, 1H), 2.64–2.54 (m, 1H), 1.36 (d, 3H, *J* = 6.5 Hz). ^{13}C NMR (DMSO, 75 MHz): δ 198, 173.1, 167.4, 163.7, 140, 138, 136.3, 114.5, 111.7, 102.1, 74.9, 43.9, 41.6, 19.6. IR (Neat): ν 3424, 2255, 2128, 1739, 1650, 1376 cm^{-1}. MS(LCMS): *m*/*z* 263 (M+ 1)$^+$. HRMS calcd for $C_{14}H_{15}O_4$: 263.0919. Found: 263.0916.