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An expedient route for the practical synthesis of pachastrissamine (jaspine B) starting from 3,4,6-tri-*O*-benzyl-D-galactal☆

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Abstract—A practically efficient stereoselective synthesis of pachastrissamine (jaspine B) is described starting from 3,4,6-tri-*O*-benzyl-D-galactal in eight steps and 11% overall yield.

1. Introduction

Saturated oxygenated heterocycles, especially tetrahydrofurans (THFs), have received attention due to their frequent occurrence in many bioactive natural products such as annonaceous acetogenins,[1] lignans,[2] polyether antibiotics,[3] and several groups of macrodiolides.[4] Owing to their diverse bioactivities[5] such as immuno-suppressive, antitumor, pesticidal, antiprotozoal, antifeedant, anthelmintic, and antimicrobial agents, the syntheses of substituted tetrahydrofurans[6] and the total syntheses of natural products containing this structural unit have been the focus of many research groups.

Consequently, we have accomplished a novel and very efficient method for the stereoselective synthesis of trisubstituted THF derivatives, starting from enantiopure glycal derived 2,3-epoxy alcohols.[7] In addition, we have also reported a consecutive approach to the synthesis of trisubstituted THF domains starting from glycal derived allylic alcohols in a single step in acceptable yields.[8]

Herein, we report the application of our method to the synthesis of a marine natural product jaspine B (Fig. 1). This anhydrosphingosine derivative was first isolated from the Okinawan marine sponge *Pachastrissa* sp. by Higa et al. in 2002 and found to possess cytotoxicity at a level of

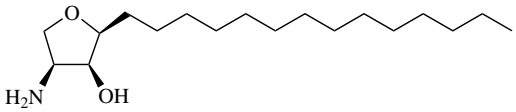

Figure 1. Pachastrissamine (jaspine B).

IC_{50} 0.01 μg/mL against P388, A549, HT29 and MeL28 cell lines.[9] In 2003, Debitus et al. isolated the same natural product from a different sponge, *Jaspis* sp., and named it as jaspine B.[10] Preliminary bioassay studies conducted by Du et al. showed that jaspine B presents strong inhibition activities against human MDA231, HeLa, and CNE cell lines,[11] indicating a potential usage in various cancer treatments. Moreover, the structural simplicity of this natural product coupled with its biological activity sparked great interest in the synthetic community which, to date, has culminated in eight synthesis[11,12] of jaspine B along with one synthesis of truncated jaspine B.[13]

However, the available literature methods for the synthesis of jaspine B involve either expensive catalysts such as Grubb's catalyst,[12b] unnatural (−)-diethyl tartrate[12e] or lengthy steps. Although the synthesis of jaspine B as reported by Overkleeft and co-workers[12d] can be completed in three steps, the starting material D-*ribo*-phytosphingosine, itself, has to be prepared from 3,4,6-tri-*O*-acetyl-D-galactal in nine steps, is highly expensive and less widely available. Among the other reported methods, the shortest route for its synthesis involved 10 steps starting from Garner's aldehyde[12a] and xylose,[11,12c] respectively.

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The basic requirements for cost-effective and efficient synthesis are the choice of a proper starting material that requires minimal protection–deprotection manipulations, a high level of stereocontrol, and less purification steps. Our method for the stereoselective synthesis of jaspine B involves 8 steps starting from most versatile starting material, 3,4,6-tri-*O*-benzyl-D-galactal, which can be easily synthesized in laboratory on a multigram scale from D-galactose.

From the retrosynthetic prospective shown in Figure 2, we planned to take advantage of our previously developed methodology[8] for constructing the THF moiety in jaspine B. The retrosynthetic disassembly of jaspine B furnishes the trisubstituted THF **2**, which is envisaged to be obtained by intramolecular asymmetric ring opening (ARO) of allylic alcohol **3** under Sharpless asymmetric epoxidation conditions and by some additional protecting group manipulations. Progenitor **3** can be easily obtained from widely available 3,4,6-tri-*O*-benzyl-D-galactal.

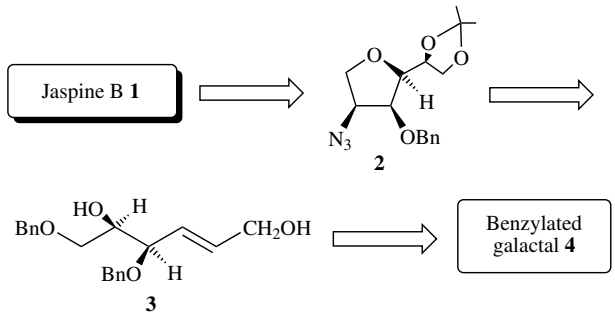


Figure 2. Retrosynthetic pathway.

2. Results and discussion

The synthesis was initiated with the readily accessible 3,4,6-tri-*O*-benzyl-D-galactal, which on Perlin hydrolysis[14] provided the α,β-unsaturated aldehyde **5**. Without any purification, aldehyde **5** was reduced to **3** in 65% (for two steps) following the procedure of Luche.[15] According to our previously established procedure,[8] the enantiopure allylic alcohol **3** was subjected to the intramolecular asymmetric ring opening (ARO) reaction under Sharpless asymmetric epoxidation conditions (1.0 equiv $Ti(O\text{–}i\text{-}Pr)_4$, 1.2 equiv (+)-diethyl tartrate (DET) and 2.0 equiv *t*-BuOOH) followed by subsequent isopropylidene protection of the diol in a consecutive fashion to afford THF domain **6** (48% yield) with three contiguous stereocenters in a single step (Scheme 1). With the required THF domain in hand, the synthesis of the natural product was embarked upon.

The esterification of the free hydroxyl group of THF domain **6** by using methane-sulfonyl chloride and triethyl amine in dry CH_2Cl_2 underwent smoothly, but the successive treatment of the crude mesylate **7** with excess of sodium azide in DMF at 120 °C for 48 h furnished azide **2** in only 30% (for two steps) along with 15% of elimination product and 40% unreacted mesylate.

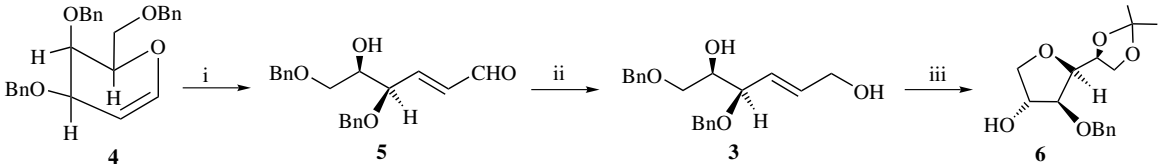
Here, the low yield of **2** can be attributed to the poor solubility of sodium azide in organic solvents. Even the use of NH_4Cl as an additive in the reaction did not show much impact on the yield of **2**. However, a significantly higher yield of the azide was achieved by the simple addition of a catalytic amount of the phase-transfer-catalyst Bu_4NCl, since it renders the NaN_3 significantly more soluble.[16] Thus, with inversion of configuration, mesylate-ester **7** was converted into azide **2** at 120 °C in DMF in 62% yield starting from **6**, along with 5% of elimination product (Scheme 2).

Having attained the required stereochemistries in the THF ring, the attachment of the alkyl side chain was undertaken. By sequential hydrolysis–oxidation–Wittig olefination (SHOWO),[17] hydrolysis–oxidation by 1.3 equiv of H_5IO_6 and Wittig olefination by tridecanylidene triphenyl phosphorane,[18] **2** was successfully transformed into **9**[11,12c] (diastereomeric mixture of *E* and *Z* isomers) in 82% yield via aldehyde **8**[11,12c] while keeping the required C-14 side chain (Scheme 2).

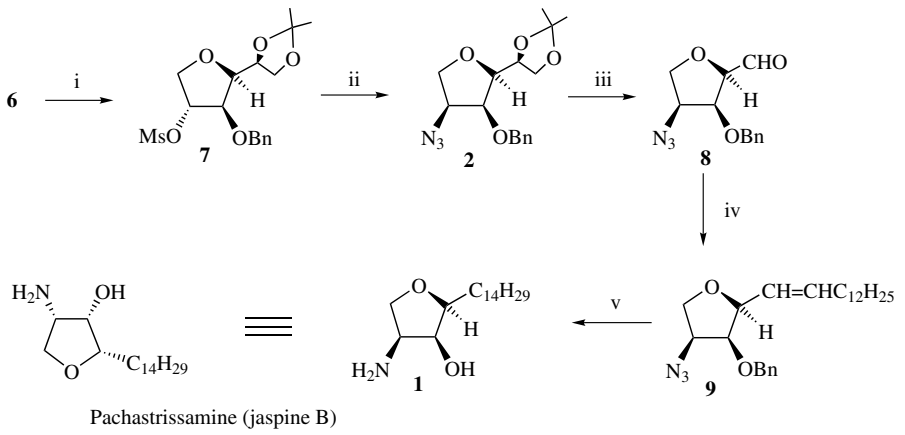
The attempted cleavage of C2 benzyl, reduction of both C3 azides and unsaturation of the side chain in **9** in a single step by hydrogenation reaction using Pd/C or $Pd(OH)_2/C$ at both atmospheric and high pressure up to 70 psi were unsatisfactory. Instead, the safer, cost-effective catalytic transfer hydrogenolysis[19] of **9** with 10% Pd/C and ammonium formate in refluxing methanol under a positive argon atmosphere for 18 h furnished target compound **1**, jaspine B, as a single isomer in 72% yield.

3. Conclusions

In conclusion, we have described a short, efficient, and straightforward synthesis of cytotoxic anhydro-phytosphingosine, Pachasstrisamine (jaspine B), in eight steps and 11% overall yield, starting from 3,4,6-tri-*O*-benzyl-D-galactal, involving intramolecular asymmetric ring opening



Scheme 1. Stereoselective synthesis of THF domain: Reagents and conditions: (i) $HgSO_4$ (cat.), 0.01 N H_2SO_4, 1,4-dioxane, 0 °C→rt, 8 h, (ii) $NaBH_4$ (0.5 equiv), $CeCl_3{\cdot}7H_2O$ (1.0 equiv), EtOH, 0 °C→rt, 3 h, 65% for two steps; (iii) $Ti(O\text{–}i\text{-}Pr)_4$ (1.0 equiv), L-(+)-DET (1.2 equiv), *t*-BuOOH (2.0 equiv), MS 4 Å, CH_2Cl_2, −25 °C→0 °C 2.5 h, satd citric acid in acetone, 2 h, 48%.



Scheme 2. Stereoselective synthesis of jaspine B **1**: Reagents and conditions: (i) MsCl, Et_3N, CH_2Cl_2, 0 °C→rt, 1.5 h; (ii) NaN_3, Bu_4NCl (cat.), DMF, 120 °C, 3 days, 62% for two steps; (iii) H_5IO_6 (1.3 equiv), EtOAc, 3 h; (iv) $C_{13}H_{27}PPh_3^+Br^-$, *n*BuLi, dry THF, −78 °C, Ar, 82% for two steps; (v) HCO_2NH_4, MeOH, Pd/C, reflux, 18 h, 72%.

of 2,3-epoxy alcohol as a pivotal step. The above method requires naturally occurring, inexpensive and easily available (+)-diethyl tartrate for the Sharpless asymmetric epoxidation. The importance of the work lies in the fact that this procedure not only allows easy access to some unnatural diastereoisomers which are hitherto unreported, by changing the glycal and chiral auxiliary, but also leads to significant waste minimization due to the fewer number of purification steps and thus can be compared favorably to previously described synthetic routes. The synthesis of the diastereoisomers along with its activity will be published elsewhere.

4. Experimental

4.1. General

DCM was dried over anhydrous calcium chloride overnight and distilled over phosphorus pentoxide. THF was freshly distilled from sodium/benzophenone, while ethyl acetate was distilled and dried over molecular sieves overnight. All reactions in non-aqueous solvents were conducted in oven-dried or flame-dried glassware under a positive pressure argon, with magnetic stirring. Ti(O–*i*-Pr)$_4$, (+)-diethyltartrate, 6.0 M solution of *t*-BuOOH in nonane, 1.6 M solution of *n*BuLi in hexane, ammonium formate were purchased from Aldrich chemical co., whereas **4** was synthesized in laboratory.

All the products were characterized by ^1H, ^{13}C, IR, ESI-MS, and EI-HRMS (C, H, O). Analytical TLC was performed using 2.5 × 5 cm plates coated with a 0.25 mm thickness of silica gel (60F-254), and visualization was accomplished with $CeSO_4$, or in some cases 30% (v/v) H_2SO_4 in MeOH and subsequent charring over a hot plate. The ^1H and ^{13}C NMR are recorded with Bruker DRX 300 spectrometers for solution in $CDCl_3$ or CD_3OD. Chemical shifts were given in parts per million downfield from internal standard Me_4Si. Carbon atom types (CH, CH_2, CH_3) were determined by DEPT pulse sequence. Yields refer to pure compounds after chromatography unless and otherwise mentioned. IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu Spectrophotometers. Mass spectra were recorded on a JEOL JMS-600H high-resolution spectrometer using EI mode at 70 eV. Optical rotations were determined on an Autopol III polarimeter using a 1 dm cell at 28 °C in chloroform/methanol as the solvent; concentrations mentioned are in g/100 mL.

4.1.1. (2*S*,3*S*,4*S*,5*R*)-1,2-*O*-Isopropylidine-3,6-anhydro-4-*O*-benzyl-5-*O*-methane-sulfonyl-D-galactitol 7. To a solution of alcohol **6** (400 mg, 1.36 mmol) in dry CH_2Cl_2 (10 mL), Et_3N (0.47 mL, 3.40 mmol) was added at 0 °C. After 5 min of stirring, a solution of methane-sulfonyl chloride (0.13 mL, 1.63 mmol) in dry CH_2Cl_2 (3 mL) was added dropwise and the reaction mixture was allowed to warm up to room temperature. After 1.5 h of stirring, the reaction was quenched by a saturated solution of $NaHCO_3$. The organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and the solvent was evaporated and used as such for the next step.

Purification of a small amount of crude product by column chromatography for data afforded pure mesylate-ester **7** as a white shiny solid; $[\alpha]_D = +12.0$ (*c* 0.05, $CHCl_3$); R_f 0.38 (3/7 EtOAc/hexane); IR (KBr, cm^{-1}): 3032, 2943, 1597, 1459, 1354; ^1H NMR (300 MHz, $CDCl_3$): δ 1.39 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.01 (s, 3H, SO_2CH_3), 3.94–4.00 (m, 2H), 4.04 (dd, 1H, $J = 3.6$, 7.1 Hz), 4.11 (dd, 1H, $J = 6.2$, 8.4 Hz), 4.22 (d, 1H, $J = 4.2$ Hz), 4.25–4.27 (m, 1H), 4.35 (dd, 1H, $J = 6.1$, 13.2 Hz), 4.72 (br s, 2H, CH_2Ph), 5.13 (d, 1H, $J = 4.2$ Hz), 7.31–7.38 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.4 (CH_3), 26.7 (CH_3), 38.5 (SO_2CH_3), 67.0 (CH_2), 71.5 (CH_2), 72.8 (CH_2), 72.9 (CH), 81.4 (CH), 81.6 (2 × CH), 109.3 (qC), 128.3 (ArC), 128.4 (ArC), 128.8 (ArC), 137.6 (qC) mass (ESI-MS) *m*/*z* 372; found 373 $[M+1]^{+\cdot}$, 395 $[M+Na]^{+\cdot}$. DART-HRMS: (M+H) calcd for $C_{17}H_{24}O_7S$+H, 373.13210; measured 373.13250, mass difference 0.41 (mmu).

4.1.2. (2*S*,3*S*,4*S*,5*S*)-1,2-*O*-Isopropylidine-3,6-anhydro-4-*O*-benzyl-5-azido-D-galactitol 2. To the solution of the crude mesylate **7** (506 mg, 1.36 mmol) in DMF (15 mL) were added NaN_3 (530 mg, 8.16 mmol) and Bu_4NCl (catalytic,

$\leqslant$0.01 g) and stirred at 120 °C for 3 days. DMF was removed under reduced pressure, and the reaction mixture washed with H_2O and the aqueous phase was re-extracted with EtOAc (3×15 mL) until TLC showed no traces of azide. The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated to yield **2** (269 mg, 62%) as a syrup; $[\alpha]_D = +47.8$ (*c* 0.138, $CHCl_3$); R_f 0.73 (3/7 EtOAc/hexane); IR (neat, cm^{-1}): 2934, 2105, 1596, 1457, 1352; ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.83 (td, 1H, $J = 4.6$, 7.3 Hz), 3.90–4.02 (m, 4H), 4.10 (dd, 1H, $J = 6.3$, 8.5 Hz), 4.22 (t, 1H, $J = 4.2$ Hz), 4.37 (dd, 1H, $J = 6.2$, 13.3 Hz), 4.76 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.84 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 7.33–7.46 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7 (CH_3), 27.1 (CH_3), 61.8 (CH), 67.3 (CH_2), 69.0 (CH_2), 73.8 (CH), 74.6 (CH_2), 79.8 (CH), 82.5 (CH), 109.3 (qC), 128.3 (ArC), 128.5 (ArC), 128.7 (ArC), 137.9 (Ar qC) mass (ESI-MS) *m*/*z* 319; found 342 $[M+Na]^{+\cdot}$.

4.1.3. Synthesis of olefin 9. A solution of azide acetonide **2** (130 mg, 0.40 mmol) and periodic acid (112 mg, 0.49 mmol) in 15 mL of dry ethyl acetate was allowed to stir for 1.5 h, then filtration and evaporation under reduced pressure afforded a colorless syrup of aldehyde **8** (>98% pure from NMR) which was immediately used in the next step.

Compound **8**; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98–4.08 (m, 3H), 4.29 (dd, 1H, $J = 2.4$, 7.2 Hz), 4.50 (dd, 1H, $J = 4.5$, 6.9 Hz), 4.66, 4.71 (2d, 2H, $J = 11.7$ Hz, CH_2Ph), 7.33–7.39 (m, 5H, ArH), 9.66 (br d, 1H, $J = 4.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 61.4 (CH), 70.8 (CH_2), 74.1 (CH_2), 81.8 (CH), 82.8 (CH), 128.3 (ArC), 128.6 (ArC), 128.9 (ArC), 136.9 (Ar qC), 200.4 (ald).

Aldehyde **8** dissolved in 5 mL of dry THF was added to orange colored solution of a freshly prepared ylide [337 mg (0.60 mmol) of phosphonium salt and 0.42 mL (0.65 mmol) of 1.6 M *n*-BuLi] dissolved in 5 mL of dry THF under Ar at −78 °C, which was stirred for 20 min. The solution was allowed to stir for an additional 30 min, and warmed to room temperature. The reaction mixture was then quenched with a saturated aqueous solution of NH_4Cl (5 mL) and extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and the solvent was removed. The residue was purified by column chromatography with EtOAc/hexane (1:49) to give a mixture of **9*E*** and **9*Z***; R_f 0.81 (1/4 EtOAc/hexane); IR (neat, cm^{-1}): 2926, 2854, 2104, 1592, 1460 1350; ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.25 (br s, 20H), 2.03–2.13 (m, 2H), 3.87–3.96 (m, 3H), 4.10 (t, 1H, $J = 4.8$ Hz), 4.62–4.72 (m, 3H), 5.64–5.74 (m, 2H) 7.28–7.36 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 23.0, 28.2, 29.7, 29.8, 30.0 (2C), 30.5, 32.3, 62.0, 69.1, 73.7, 76.3, 80.9, 125.5, 128.1, 128.2, 128.8, 135.5, 137.8.

4.1.4. Synthesis of pachastrissamine 1 (jaspine B). A mixture of compounds **9** (55 mg, 0.13 mmol), ammonium formate (420 mg, 6.65 mmol), and 10% Pd/C (20 mg) in dried MeOH (10 mL) was stirred under an Ar atmosphere at reflux for 18 h. The mixture was filtered and concentrated. Purification of the resulting residue by $CHCl_3$/MeOH/aq NH_4OH (89:10:1) as eluent afforded target compound **1** as an offwhite amorphous solid (28 mg, 72%). $[\alpha]_D = +13.3$ (*c* 0.03, EtOH), $[\alpha]_D = +8.5$ (*c* 0.047, MeOH), {lit.[9] $[\alpha]_D = +18$ (*c* 0.1, EtOH), lit.[12d] $[\alpha]_D^{22} = +4.8$ (*c* 1.0, MeOH)}; R_f 0.18 (3/17 MeOH/$CHCl_3$); IR (KBr, cm^{-1}): 2916, 2848, 1654, 1631, 1583, 1070, 831, 719; ^1H NMR (300 MHz, CD_3OD): δ 0.89 (t, 3H, $J = 6.8$ Hz), 1.28 (br s, 24H), 1.61–1.63 (m, 2H), 3.49–3.69 (m, 2H), 3.73–3.78 (m, 1H), 3.92 (qt, 1H), 4.01–4.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$/CD_3OD) δ 14.5, 23.1, 26.5, 29.1, 29.3, 29.7, 30.1, 32.3, 34.0, 54.4, 70.5, 71.3, 83.5; mass (EI-MS) *m*/*z* 299, found 299 $[M]^{+\cdot}$, 300 $[M+1]^{+\cdot}$. EI-HRMS: calcd for $C_{18}H_{37}NO_2$, 299.2824, measured 299.2824, error, 0.0 (mmu).

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