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Total synthesis of (−)-petrosiol E

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ABSTRACT

(−)-Petrosiol E, a metabolite of sponge *Petrosia strongylata*, has been synthesized in 32% overall yield from cheap natural D-xylose in 10 steps. Our strategy provides an efficient way for the total synthesis of other petrosiol members, featuring the three contiguous stereogenic centers are easily constructed from D-xylose chiral template.

1. Introduction

Diyne polyol backbone is a unique unit found in a number of biologically active natural products.[1] Petrosiols A–E (**1**–**5**), naturally occurring novel neurotrophic diyne tetraols, have been isolated recently from an Okinawan marine sponge *Petrosia strongylata* by Ojika's group and found to induce nerve growth factor (NGF-like) neuronal differentiation of PC12 cells.[2] The structures of petrosiols were elucidated based on extensive spectroscopic analyses. The petrosiols A–E (**1**–**5**) are comprised of the similar unusual diyne tetraol skeletons with different side-chain lengths. The consistent sign of their specific optical rotations, the similar NMR data around the triol moieties, and the chemical derivatization studies indicated that all the petrosiols share the same stereochemistry. The relative stereochemistry of the petrosiols was established by derivatization of petrosiol C (**3**),[2] and the absolute configurations were examined by the modified Mosher's method. Detailed biological analyses demonstrated that petrosiols may be useful for the prevention and treatment of vascular diseases such as restenosis and atherosclerosis[3] (Fig. 1).

Because of their unique structures, interesting biological activities, and limited availability, petrosiols represent attractive targets for total synthesis. In continuation of our efforts toward the total synthesis of biologically active natural products based on carbohydrate skeletons,[4] we launched a stereoselective total synthesis of natural petrosiols, taking petrosiol E (**5**) as our first target. During our efforts, Srihari et al. reported the first total synthesis of petrosiol D (**4**).[5] In their report, petrosiol D (**4**) was prepared from (+)-diethyl L-tartrate with an overall yield of 4.7% in 17 steps, employing Sharpless asymmetric epoxidation, base-induced elimination of chiral epoxy halides, and Cadiot–Chodkiewicz coupling

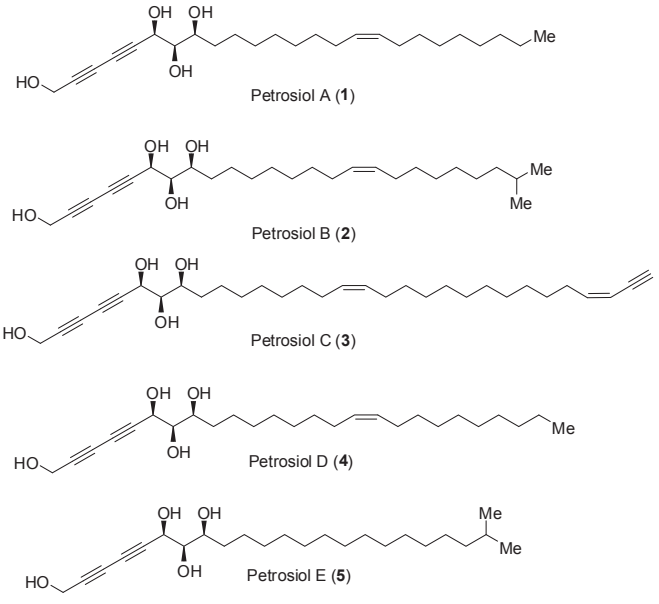

Fig. 1. Structures of petrosiol A–E (**1**–**5**).

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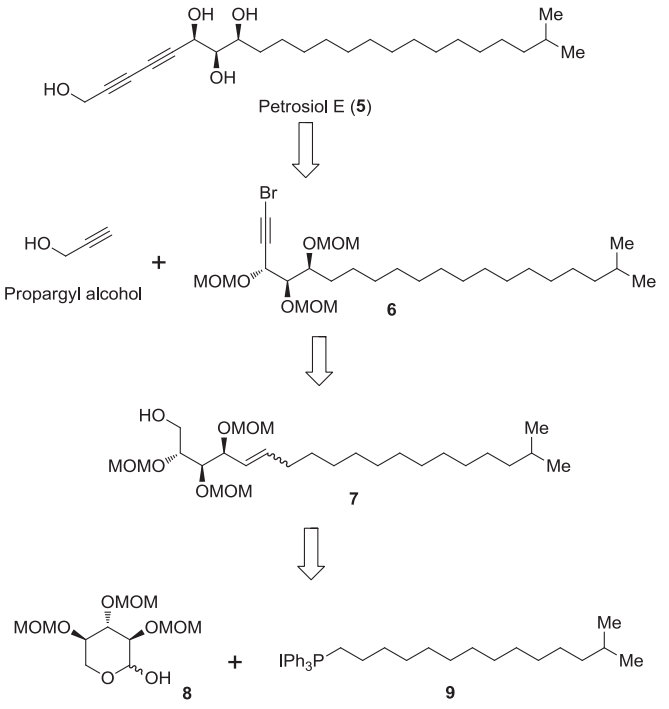
as the key steps. We realized that the chiron approach represents probably the better way for making biologically active petrosiols if the characteristic three contiguous oxy-stereocenters in petrosiols could be derived from natural carbohydrate chiral templates. Here, we report the first total synthesis of petrosiol E using readily available D-xylose as the chiral template.

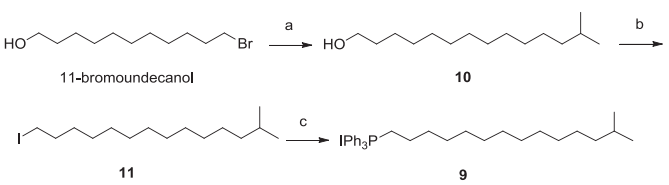
Retrosynthetic analysis of (−)-petrosiol E is shown in Scheme 1. The crucial diyne tetraol skeleton could be installed by coupling of the 1-bromoalkyne **6** with propargyl alcohol via copper-catalyzed Cadiot–Chodkiewicz reaction. The key intermediate **6** could be obtained from alkene **7** via a multi-step sequence: hydrogenation of alcohol **7**, followed by oxidation, Wittig reaction, and base-induced elimination would furnish the desired 1-bromoalkyne **6**. Alkene **7** could be obtained by chain elongation of the known MOM-protected D-xylose **8**[6] with the phosphonium salt **9**, which could be accessible readily from D-xylose and 11-bromoundecanol, respectively. Taking advantages of its excellent stabilities under strong base treatment and Pd-catalyzed hydrogenation conditions, methoxymethyl (MOM) was selected to protect hydroxyl groups of D-xylose and could be removed eventually under acid conditions.



Scheme 1. Retrosynthetic analysis of (−)-petrosiol E (**5**).

2. Results and discussion

The synthetic sequence commenced with the coupling of isobutylmagnesium bromide and commercially available 11-bromoundecanol in the presence of dilithium tetrachlorocuprate (Li_2CuCl_4).[7] The primary alcohol **10** was transformed into alkyl iodide **11** (Scheme 2) and then the intermediate was treated with neat PPh_3 at 100 °C to deliver the phosphonium salt **9** in 96% overall yield for three steps.



Scheme 2. Reagents and conditions: (a) Me_2CHCH_2MgBr, Li_2CuCl_4, anhydrous THF, −78 °C to rt, overnight; (b) I_2, PPh_3, imidazole, anhydrous toluene, 0–60 °C, 2 h; (c) PPh_3, 100 °C, 2 h, 96% (for three steps).

The known MOM-protected D-xylose derivative **8** was prepared from D-xylose according to a published procedure[6] in 62% of overall yield for three steps. Wittig olefination of the hemiacetal **8** and the phosphonium salt **9** was thus pursued. However, the expecting chain elongation at the anomeric carbon of D-xylose turned out to be more difficult than we expected. As summarized in Table 1, treatment of **8** with the phosphonium salt **9** in the presence of various strong bases (*t*-BuOK, *n*-BuLi, t-BuLi, LHMDS), resulted in the recovery of starting material (entries 1, 2, 4) or led to the decomposition of **8** (entry 3). The best result for the chain elongation was finally achieved through a reaction of **8** with the ylide, generated in situ by **9** and lithium hexamethyldisilazide (LHMDS) in anhydrous toluene at 0–50 °C (entry 5), afforded the desired alkene **7** in 92% yield.

Table 1
Reagents and conditions for the formation of **7**[a]

Entry	Base	Temperature	Solvent	Yield (%)
1	*t*-BuOK	0 °C to rt	THF	No reaction
2	*n*-BuLi	−78 °C to rt	Toluene	No reaction
3	*n*-BuLi	0 °C to 50 °C	Toluene	Decomposition
4	LHMDS	−78 °C to rt	Toluene	No reaction
5	LHMDS	0 °C to 50 °C	Toluene	92

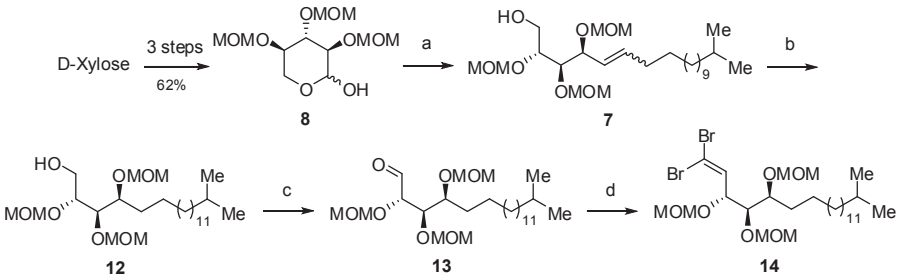
[a] Detailed procedures are provided in Experimental section.

Pd-catalyzed hydrogenation of alkene **7** in methanol at room temperature saturated the double bond in excellent yield. The resulted alcohol **12** was oxidized with pyridinium dichromate (PDC) to yield aldehyde **13** smoothly. It should be noted that Dess–Martin periodinane[8] oxidation of **12** under various conditions resulted in the recovery of starting material. Possibly, the steric hindrance of the tri-MOM groups shielded the free hydroxyl group from the bulky periodinane attacking.

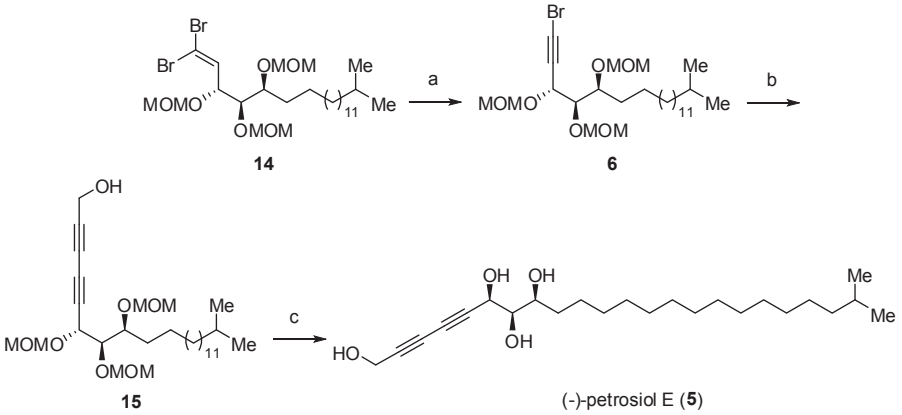
Transformation of aldehyde **13** to 1-bromoalkyne **6** also proved to be more challenging than we initially anticipated. The Corey–Fuchs dibromoolefination was first explored.[9] Unfortunately, treatment of **13** with CBr_4/PPh_3 led to the decomposition of **13**, and no detectable 1,1-dibromoalkene was formed. Apparently, an in situ generated dibromotriphenylphosphine (Ph_3PBr_2) caused aldehyde decomposition.[10] The Seyferth–Gilbert homologation strategy was also examined, but fruitless.[11] Thus, an alternative strategy of making **6** was designed with the help of HBr elimination. The dibromoalkene **14** was obtained in good yield through a Wittig-type reaction of aldehyde **13** and dibromomethyltriphenylphosphonium bromide (Scheme 3).[12] It was reported that TBAF was an efficient base for this dehydrobromination in polar aprotic solvents.[13] Accordingly, treatment of **14** with an excessive of TBAF in DMF should give the corresponding 1-bromoalkyne **6**. However, in our case, TBAF led to the terminal alkyne instead of the desired 1-bromoalkyne **6**. To our delight, NaH in THF was found more reliable, furnishing the 1-bromoalkyne **6** in excellent yield.[14] Cadiot–Chodkiewicz coupling of **6** with propargyl alcohol produced the desired conjugated diyne **15**.[15] Finally, global deprotection of **15** with 3 N HCl afforded the target natural product petrosiol E (**5**)[16] (Scheme 4). All the spectroscopic data and the specific optical rotation for our synthetic petrosiol E were in good agreement with those reported for the natural product {$[\alpha]_D^{25}$ −2.0 (*c* 0.06, MeOH); Ref. 2: $[\alpha]_D^{25}$ −1.0 (*c* 0.06, MeOH)}[2] (see Supplementary data).

3. Conclusions

In conclusion, we have achieved the first total synthesis of (−)-petrosiol E starting from the chiral template D-xylose in 10



Scheme 3. Reagents and conditions: (a) **9**, LHMDS, anhydrous toluene, 0–50 °C, overnight; (b) Pd/C, H_2, MeOH, rt, overnight, 89% (for two steps); (c) PDC, AcONa, MS-4 Å, CH_2Cl_2, reflux, 3 h; (d) $(Ph_3PCHBr_2)Br$, *t*-BuOK, anhydrous THF, 0 °C to rt, 2 h, 81% (for two steps).



Scheme 4. Reagents and conditions: (a) NaH, anhydrous THF, rt, overnight; (b) propargyl alcohol, CuCl, $NH_2OH{\cdot}HCl$, Et_2O, *n*-$BuNH_2$, H_2O, 0 °C to rt, 30 min, 76% (for two steps); (c) 3 N HCl, EtOH, 80 °C, 3 h, 95%.

steps with an overall yield of 32%. The current work also confirmed the absolute stereochemistry of **5** based on physical data agreements from both synthetic and natural samples. Because of its compactness and efficiency, our strategy is attractive for the facile preparation of structurally similar natural products. Further efforts on the total synthesis of other petrosiols and the bioactivity evaluations are currently underway in our laboratory.

4. Experimental section

4.1. General

All commercially available reagents were used without further purification. All anhydrous solvents were purified according to standard procedures before use. Reactions were monitored by thin-layer chromatography (TLC) on silica gel F_{254} plates. Flash chromatography (FC) was performed using silica gel (200–300 mesh) according to the standard protocol. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-III 400 MHz (100 MHz for ^{13}C NMR) spectrometer. High-resolution mass spectrometry (HRMS) data were measured with a Bruker microTOF-Q II mass spectrometer. Optical rotations were recorded in either a 5-cm microcell or a 2.5-cm microcell.

4.2. Iodo(13-methyltetradecyl)triphenylphosphorane (9)

To a stirred solution of 11-bromoundecanol (10 g, 40 mmol) in anhydrous THF (100 mL) was added a solution of isobutylmagnesium bromide (1 mol/L in THF, 148 mL, 148 mmol), followed by a solution of Li_2CuCl_4 (0.1 mol/L in THF, 5 mL, 0.5 mmol) at −78 °C under N_2 atmosphere. The resulting mixture was warmed to room temperature and stirred overnight. After the reaction mixture was quenched with saturated aq NH_4Cl, it was extracted with EtOAc (3×30 mL). The combined organic layers were washed with water, saturated aq $NaHCO_3$ and brine, then dried over Na_2SO_4, and concentrated under reduced pressure to give the crude alcohol **10** as a white solid, which was used for the next reaction without further purification.

To a vigorously stirred solution of the crude alcohol **10**, triphenylphosphine (15.72 g, 60 mmol), and imidazole (8.16 g, 120 mmol) in anhydrous toluene (300 mL) was added iodine (15.24 g, 60 mmol) at 0 °C. The resulting mixture was stirred at 60 °C for 2 h. After TLC showed that all the starting alcohol had disappeared, to the mixture was added methanol (5 mL). After full consumption of triphenylphosphine judged via TLC, the mixture was cooled to room temperature, washed with saturated aq $Na_2S_2O_3$, and extracted with Et_2O. The combined organic layer was washed with brine, dried, and concentrated under reduced pressure. The residue was eluted with petroleum ether on a short silica gel column to give the colorless crude iodide **11** as oil, which was used for the next reaction without further purification.

A mixture of the above iodide **11** and triphenylphosphine (83.84 g, 320 mmol) was fused at 100 °C under N_2 atmosphere. After being stirred for 2 h at the same temperature, the reaction mixture was cooled to room temperature, dissolved in MeCN (300 mL), and washed with petroleum ether (450 mL×12 times). The MeCN layer was concentrated under reduced pressure to give the crude phosphonium salt **9** (23.1 g, 96% for three steps) as a yellow solid, which could be used for the next reaction without further purification; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.87 (m, 9H), 7.68–7.73 (m, 6H), 3.74 (m, 2H), 1.64 (m, 5H), 1.46–1.56 (m, 1H), 1.11–1.22 (m, 17H), 0.85 (d, J=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (3C), 133.9 (3C), 133.8 (3C), 130.8 (3C), 130.7 (3C), 118.7 (2C), 117.8, 39.2, 29.3–30.7 (10C), 28.1, 27.5, 22.8, 22.7; ESI-HRMS calcd for $C_{33}H_{46}P$ ($[M-I]^+$) 473.3331, found 473.3346.

4.3. (2*R*,3*R*,4*S*)-2,3,4-Tris(methoxymethoxy)-18-methylnonadecan-1-ol (12)

The phosphonium salt **9** (4.14 g, 6.90 mmol) was azeotropically dried with toluene and further dried by heating to 50 °C under vacuum for 4 h. The salt was cooled to room temperature, backfilled with N_2, and dissolved in anhydrous toluene (30 mL). To the resultant solution was added dropwise LHMDS (1.0 mol/L in THF, 6.90 mL, 6.90 mmol) at 0 °C under N_2 atmosphere. The resulting red mixture was stirred at room temperature for 1 h. To the above mixture was added a solution of tri-*O*-methoxymethyl-D-xylopyranose **8** (778 mg, 2.76 mmol) in anhydrous toluene (10 mL), and the resulting mixture was stirred at 50 °C overnight. At the end of which time, the reaction mixture was quenched with saturated aq NH_4Cl and extracted with EtOAc (3×20 mL). The extracts were washed with brine, dried, and concentrated under reduced pressure to give the crude alkene **7**, which was used for next reaction without further purification.

A mixture of alkene **7** and 10% Pd/C (294 mg, 0.276 mmol) in methanol (10 mL) was stirred vigorously at room temperature under H_2 atmosphere overnight until all starting materials were consumed. The mixture was filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:4) to give the alcohol **12** (1.17 g, 89% for two steps) as a colorless oil; $[\alpha]_D^{25}$ 20 (*c* 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66–4.80 (m, 6H), 3.69–3.82 (m, 5H), 3.43 (s, 3H), 3.42 (s, 3H), 3.39 (s, 3H), 1.63–1.72 (m, 1H), 1.45–1.56 (m, 2H), 1.38 (m, 2H), 1.25 (m, 20H), 1.12–1.15 (m, 2H), 0.86 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 98.9, 97.9, 97.3, 80.9, 79.5, 78.6, 62.7, 56.5, 56.2 (2C), 39.3, 31.0, 29.9–30.2 (9C), 28.3, 27.7, 25.6, 23.0 (2C); ESI-HRMS calcd for $C_{26}H_{54}O_7$ ($[M+Na]^+$) 501.3762, found 501.3775.

4.4. 3(5*R*,6*R*,7*S*)-5-(2,2-Dibromovinyl)-6-(methoxymethoxy)-7-(14-methylpentadecyl)-2,4,8,10-tetraoxaundecane (14)

To a stirred solution of the alcohol **12** (350 mg, 0.732 mmol) in CH_2Cl_2 (10 mL) was added anhydrous molecular sieves (4 Å, 826 mg), sodium acetate (180 mg, 2.20 mmol), and pyridinium dichromate (826 mg, 2.20 mmol) at room temperature. After being stirred under reflux for 3 h, the mixture was eluted from a short column of silica gel with EtOAc to give aldehyde **13**, which was used for next reaction without further purification.

t-BuOK (234 mg, 2.09 mmol) was added to a solution of $(Ph_3PCHBr_2)Br$ (1.13 g, 2.20 mmol) in anhydrous THF (10 mL) at 0 °C under N_2 atmosphere. The mixture was warmed to room temperature and stirred for 30 min, followed by addition of a solution of **13** in anhydrous THF (2 mL). After 2 h, the reaction mixture was quenched with brine, and extracted with EtOAc. The combined organic layers were dried, concentrated under reduced pressure, and purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:10) to give the dibromoalkene **14** (374 mg, 81% for two steps) as a colorless oil; $[\alpha]_D^{25}$ −111 (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (d, *J*=8.8 Hz, 1H), 4.74–4.82 (m, 3H), 4.69 (dd, *J*=3.2, 6.8 Hz, 2H), 4.59 (d, *J*=6.8 Hz, 1H), 4.51 (dd, *J*=4.0, 8.8 Hz, 1H), 3.75–3.79 (m, 1H), 3.68–3.70 (m, 1H), 3.44 (s, 3H), 3.40 (s, 3H), 3.39 (s, 3H), 1.67–1.76 (m, 1H), 1.46–1.64 (m, 3H), 1.39–1.41 (m, 2H), 1.25 (m, 19H), 1.14–1.15 (m, 2H), 0.86 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 98.4, 97.6, 94.9, 92.7, 79.8, 78.7, 76.4, 56.6, 56.4, 56.2, 39.3, 31.3, 29.9–30.2 (9C), 28.2, 27.7, 25.3, 22.9 (2C); ESI-HRMS calcd for $C_{27}H_{52}Br_2O_6$ ($[M+Na]^+$) 655.2005, found 655.2006.

4.5. (6*R*,7*R*,8*S*)-6,7,8-Tris(methoxymethoxy)-22-methyltricosa-2,4-diyn-1-ol (15)

To a stirred solution of the dibromoalkene **14** (54 mg, 0.086 mmol) in anhydrous THF (1 mL) was added 60% sodium hydride (34 mg, 0.86 mmol) as a solid at 0 °C. The resulting mixture was warmed to room temperature and stirred overnight. After the reaction mixture was quenched with saturated aq NH_4Cl, it was extracted with EtOAc. The combined organic layers were washed with brine, dried, and concentrated under reduced pressure to give the crude 1-bromoalkyne **6**, which was used for the next reaction without further purification.

To a stirred 30% *n*-$BuNH_2$ aqueous solution (5 mL) was added CuCl (0.2 mg, 0.002 mmol) at room temperature, resulted in the formation of a blue solution immediately. A few crystals of hydroxylamine hydrochloride were added until the blue color disappeared. The resulting colorless solution indicated the present of Cu (I) salt. A solution of propargyl alcohol (50 μL, 0.86 mmol) in Et_2O (0.5 mL) was added to the solution at room temperature, yielding a yellow acetylide suspension, which was immediately cooled to 0 °C. A solution of the 1-bromoalkyne **6** in Et_2O (2 mL) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 30 min. More crystals of hydroxylamine hydrochloride were added throughout the reaction to prevent the reaction mixture from turning blue or green. The reaction mixture was extracted with Et_2O (3×15 mL). The combined organic layers were dried, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:6) to give the diyne **15** (34 mg, 76% for two steps) as a colorless oil; $[\alpha]_D^{25}$ −122 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (dd, *J*=6.8, 16.4 Hz, 2H), 4.71–4.74 (m, 3H), 4.67 (d, *J*=7.2 Hz, 1H), 4.62 (d, *J*=6.8 Hz, 1H), 4.33 (s, 2H), 3.85–3.89 (m, 1H), 3.74 (dd, *J*=3.2, 7.2 Hz, 1H), 3.43 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 1.95 (br, 1H), 1.44–1.71 (m, 4H), 1.25 (m, 21H), 1.11–1.15 (m, 2H), 0.85 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 98.7, 97.1, 95.1, 80.0, 78.0, 76.3, 71.6, 70.0, 68.4, 56.7, 56.3 (2C), 51.7, 39.4, 31.3, 30.0–30.3 (9C), 28.3, 27.8, 25.7, 23.0 (2C); ESI-HRMS calcd for $C_{30}H_{54}O_7$ ($[M+Na]^+$) 549.3762, found 549.3774.

4.6. (−)-Petrosiol E (5)

To a stirred solution of the diyne **15** (28 mg, 0.053 mmol) in EtOH (2.5 mL) was added 3 N HCl aqueous solution (0.6 mL) at room temperature. The mixture was stirred at 80 °C for 3 h. After the reaction mixture was quenched with saturated aq NH_4Cl, it was extracted with EtOAC. The combined organic layers were dried, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:1) to give petrosiol E (**5**) (20 mg, 95%) as a colorless powder; $[\alpha]_D^{25}$ −2 (*c* 0.06, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD (4:1)): δ 4.46 (d, *J*=6.4 Hz, 1H), 4.26 (s, 2H), 3.76 (m, 1H), 3.44 (d, *J*=5.6 Hz, 1H), 1.13–1.66 (m, 27H), 0.87 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD (4:1)): δ 78.3, 77.6, 76.1, 71.3, 70.1, 68.9, 64.5, 50.6, 39.2, 34.2, 29.8–30.1 (9C), 28.1, 27.6, 25.9, 22.7 (2C); ESI-HRMS calcd for $C_{24}H_{42}O_4$ ($[M+Na]^+$) 417.2975, found 417.2966.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.09.030.

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