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Total synthesis of sapinofuranone A from D-ribose

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ABSTRACT

The total synthesis of sapinofuranone A has been achieved starting from naturally occurring carbohydrate D-ribose via a short and high yielding route. The key transformations include Wittig olefination, Ohira–Bestmann reaction, Sonogashira coupling. Finally acetonide deprotection and subsequent lactonization using catalytic amount of hydrochloric acid completed the total synthesis of sapinofuranone A.

1. Introduction

During recent years, butanolide and the corresponding γ-lactone motifs containing natural products are attaining significant interest due to their potent biological properties.[1] 5-Substituted dihydrofuranones, named sapinofuranone A and B (**1** and **2**), were isolated from liquid cultures of *Sphaeropsis sapinea*, a phytopathogenic fungus causing a wide range of disease symptoms on conifers (Fig. 1).

This butanolide natural product, sapinofuranone A, was isolated by Antonio Evidente and co-workers in 1999 from liquid cultures of a phytopathogenic fungus, *S. sapinea*.[2] A new strategy to extend the application of the *J*-based configuration and an application to sapinofuranone A was demonstrated by Gomez-Paloma and co-workers in 2002.[3] Intrigued by the biological properties of these 5-substituted dihyrofuranone, we got interested in the total synthesis of sapinofuranone A. In continuation to our work on the total synthesis of furanoside building blocks containing natural products[4] herein, we report the stereoselective total synthesis of a natural product sapinofuranone A in a stereoselective fashion involving easily accessible starting materials. To date, only one report on the synthesis of sapinofuranone A (**1**) exists.[5]

2. Results and discussion

The retro-synthetic analysis of compound **1** is shown in Scheme 1. It was envisioned that sapinofuranone A (**1**) could be synthesized from **12** by one-pot acetonide deprotection and simple lactonization. While in turn the diene **12** could be derived from **8** by IBX oxidation followed by Ohira–Bestmann reaction by the formation of triple bond and Sonogashira coupling and selective reduction of triple bond by Zn catalyst. Compound **8** can be obtained from **6** by Wittig olefination and reduction of conjugated double bond by $NiCl_2 \cdot 6H_2O$ and $NaBH_4$. Compound **6** could be derived from the commercially available D-ribose **4** (Scheme 1).

As shown in Scheme 2, the synthesis of the key intermediate **9** starting from the commercially available D-ribose **4** was treated with catalytic amount of H_2SO_4 and acetone, which resulted in 2,3-acetonide **5** in quantitative yields. Sequential reduction with $NaBH_4$ followed by oxidative cleavage of the diol with $NaIO_4$ provided aldehyde **6**. The aldehyde was subjected to Wittig olefination using

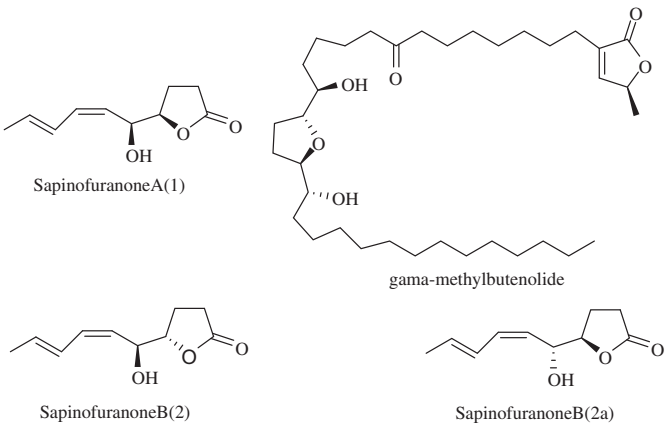

Fig. 1. Sapinofuranone A, sapinofuranone B, and related compounds.

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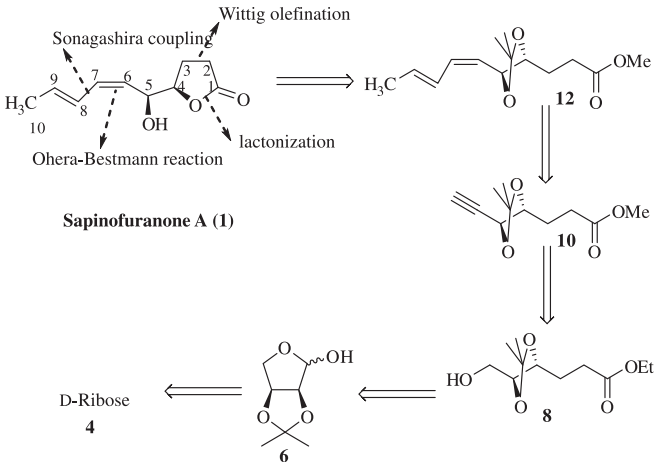
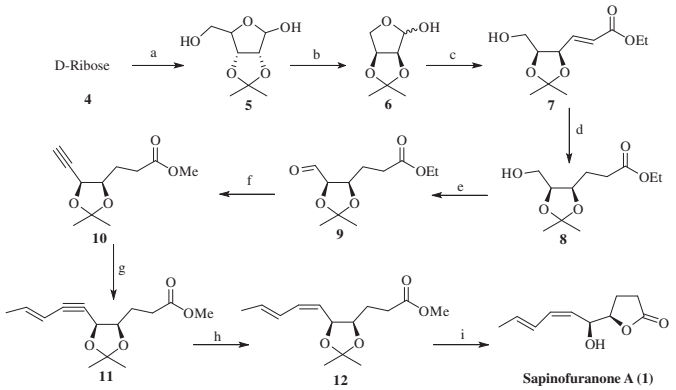


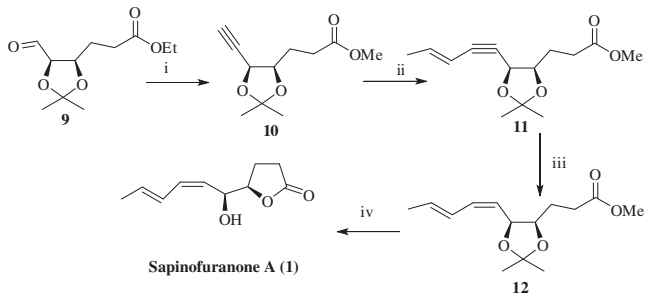
Scheme 1. Retro synthesis of sapinofuranone A.



Scheme 2. Reagents and conditions: (a) cat.H_2SO_4/acetone, 4 h; (b)(i) $NaBH_4$/MeOH, 0 °C, 2H, (ii) $NaIO_4$, $^tBuOH/H_2O$ (3/2), 12 h; (c) Ph_3PCHCO_2Et/cat.PhCOOH, CH_2Cl_2, reflux, 12 h; (d) $NaBH_4$, $NiCl_2{\cdot}6H_2O$, MeOH, 0 °C to rt, 3 h; (e) IBX, DMSO, rt, 3 h; (f) $CH_3COC{=}N_2PO(OMe)_2/K_2CO_3$, MeOH, rt, 3 h; (g) $BrCH{=}CHCH_3$, $[Pd(Ph_3P)_2Cl_2]$, CuI, piperidine, DMF, 70 °C, 4H; (h) Zn (Cu/Ag), MeOH reflux, 12 h; (i) cat.HCl/THF, rt, 6 h.

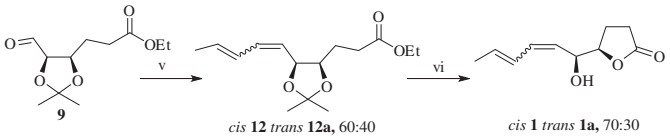
ylide to yield the fragment **7** with a yield of 89%. The conjugated double bond was reduced with catalytic amount of $NiCl_2{\cdot}6H_2O$ and $NaBH_4$ to give the compound **8** with 94.9% yield. Compound **8** oxidized with IBX in DMSO at room temperature afforded the key intermediate **9**. Compound **9** was characterized from ^1H NMR spectrum by the appearance of aldehydic proton (1H) at δ 9.67 as doublet (d, 1H, J=2.44 Hz). It was also characterized by ^{13}C NMR spectrum by the appearance of aldehydic carbonyl carbon at δ 201.8. The mass spectrum exhibited the mass value of m/z 253 $(M+Na)^+$ was in agreement with the structure. This synthetic method is regarded as the best procedure from the viewpoint of the number of steps and the overall yields and large-scale preparation conditions and has a great potential to be utilized extensively in the synthesis of the sapinofuranones.

With the key intermediate **9** in hand, we focused the synthesis of **1** (Scheme 3). Aldehyde **9** subjected to one-carbon homologation using Ohira–Bestmann reagent afforded the alkyne **10** in 75% yield. Alkyne **10** was subjected to Sonogashira coupling with *trans*-1-bromo-1-propene using Cu_2I_2, $Pd(Ph_3P)_2Cl_2$, and triethylamine to afford the desired product **11**. The compound **11** was reduced using activated Zn[6] affording the diene **12** as a single isomer, which on treatment with catalytic amount of HCl in THF underwent one-pot acetonide deprotection and lactonization to afford the target molecule sapinofuranone A in 79% yield. The ^1H NMR and ^{13}C NMR spectral data of our synthetic compound were in good agreement with the data previously reported in literature.[2]



Scheme 3. Reagents and conditions: (i) $CH_3COC{=}N_2PO(OMe)_2/K_2CO_3$, MeOH, rt, 3 h; (ii) $BrCH{=}CHCH_3$, $[Pd(Ph_3P)_2Cl_2]$, CuI, Et_3N (dry), 6H; (iii) Zn (Cu/Ag), MeOH reflux, 12 h; (iv) cat.HCl/THF, rt, 6 h.

In another approach, we obtained the following diastereomeric mixture. Toward the end, the compound **9** was subjected to Wittig olefination to furnish **12**, as expected, was non-stereoselective and led to a mixture of nearly 7/3 of diastereomers *cis* **12**: *trans* **12a** (Scheme 4). While the two diastereomers were inseparable and the mixture was treated with catalytic amount of HCl, which yielded inseparable diastereomeric mixture of sapinofuranone A (**1**). We could not find a suitable method to separate the diastereomeric mixture. We concluded that the synthetic route involving Wittig olefination of the compound **9** to target molecule sapinofuranone A (**1**) could not evade the above mentioned synthetic dead end.



Scheme 4. Reagents and conditions: (v) $CH_3CH{=}CHCH_2PPh_3Br$, LiHMDS, THF, −78 °C, 4 h; (vi) cat.HCl/THF, rt, 6 h.

3. Conclusion

In summary, we have synthesized sapinofuranone A via a short (eight steps), high yielding route (18% overall yield from commercially available D-ribose). The key transformations involved in the synthesis are Sonogashira coupling; one-pot tandem acetonide deprotection and subsequent dihydrofuranone ring formation. Our approach to the syntheses of **8** and **9** are promisingly applicable for the syntheses of other butanolide natural products of γ-lactone motifs.

4. Experimental section

4.1. General information

All reactions requiring anhydrous conditions were performed in oven-dried glassware under argon. Nuclear Magnetic Resonance (^1H and ^{13}C NMR) spectra were recorded on Varian Gemini 200, 400 or Bruker WH 300 MHz spectrometers, using tetramethylsilane (TMS) as the internal standard. Chemical shifts were expressed in (ppm) down field from TMS. IR spectra were recorded on Perkin–Elmer model 683 or 1310 spectrometers with sodium chloride optics or KBr pellets. EI Mass spectra were recoded on a VG Micromass-7070 Hz 70 eV using a direct inlet system. ESI MS were recorded on Thermo Finnigan LCQ ion trap mass spectrometer equipped with an electron spray ionization. High Resolution Mass spectra were recoded on Q STAR mass spectrometer (Applied Biosystems USA) at 5 or 7 K resolution using polyethylene glycol as an internal reference compound. Optical rotations were recorded on JASCO DIP 370 digital polarimeter. All reactions were monitored by thin layer

chromatography (TLC) employing 0.25 mm silica gel plates (60F-254, E-Merck). Column chromatography was performed using Acme silica gel (60–120 mesh). Visualization of the spots on TLC plates was achieved either by exposure to UV light, iodine vapor and by dipping the plates in phosphomolybdic acid–ceric (IV) sulfate–sulfuric acid solution (PMA solution) and heating the plates at 120 °C.

*4.1.1. (3aR,6R,6aR)-6-(Hydroxymethyl)-2,2-dimethyltetrahydrofuro [3,4-d][1,3]dioxol-4-ol (**5**).* To a stirred solution of D-ribose (**4**) (10.0 g, 66.6 mmol) in acetone (100 mL), concd H_2SO_4 (0.3 mL) was added drop wise at room temperature. And the resulting reaction mixture was stirred at room temperature for 2 h, until TLC showed complete conversion of the starting material. The reaction mixture was neutralized by addition of solid $NaHCO_3$ and filtered to remove inorganic solid. The filtrate was concentrated under reduced pressure to give colorless syrup. The residue was purified by silica gel column chromatography using hexane and ethyl acetate (30%) as the eluent to afford **5** as colorless syrup (11.7 g, 92.4%); R_f 0.4 (50% EtOAc/hexane); $[\alpha]_D^{28}$ −36.7 (*c* 1.1, acetone); IR (KBr, neat): 869, 1068, 1211, 1376, 1458, 1635, 2940, 2986, 3408; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (3H, s, CH_3), 1.49 (3H, s, CH_3), 3.74 (2H, s, *CH*$_2$OH), 4.41 (1H, s, *CH*CH_2), 4.59 (1H, d, *J*=6.04 Hz, CH), 4.84 (1H, d, *J*=5.66 Hz, CH), 5.42 (1H, s, *CH*OH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 24.5, 26.2, 63.3, 81.5, 86.5, 87.5, 102.5, 112.0; MS (ESI): *m*/*z* 213 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 213.07334. Found 213.07304.

*4.1.2. (3aS,6aS)-2,2-Dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-ol (**6**).* To a stirred solution of D-ribose monoacetonide **5** (11.0 g, 57.8 mmol) in dry methanol (70 mL), $NaBH_4$ (3.29 g, 86.8 mmol) was added in small portions at 0 °C. And the resulting reaction mixture was stirred at room temperature for 1 h until TLC showed complete conversion of starting material. Then the solvent was distilled off under reduced pressure, and then ^{t}BuOH/H_2O (90/60 mL), $NaIO_4$ (49.5 g, 231.5 mmol) were added in small portions at room temperature. And the resulting reaction mixture was stirred at room temperature for 12 h until TLC showed complete conversion of stirring material. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and neutralized by the addition of solid $NaHCO_3$ and filtered to remove inorganic solid. The filtrate was extracted into CH_2Cl_2 (2×50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh, hexane/ethyl acetate, 75/25] to obtain the title compound **6** (7.3 g, 78.9%) as an oil. R_f 0.4 (30%EtOAc/hexane); $[\alpha]_D^{28}$ −76.1 (*c* 1.3, $CHCl_3$); IR (KBr, neat): 1067, 1210, 1375, 1459, 1633, 2925, 3433; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, s, CH_3), 1.44 (3H, s, CH_3), 3.91–4.06 (2H, m, CH_2), 4.51 (1H, d, *J*=*5.66* Hz, CH), 4.77–4.81 (1H, dd, *J*=3.39, 5.66 Hz, CH), 5.35 (1H, s, *CH*OH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 24.5, 26.0, 71.6, 79.8, 85.0, 101.5, 112.1; MS (EI): *m*/*z* 183 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 183.04957. Found 183.04913.

*4.1.3. Ethyl3-((4R,5S)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate (**7**).* To a solution of compound **6** (7.1 g, 44.3 mmol) in CH_2Cl_2 (80 mL), ethoxycarbonylmethylene triphenylphosphonate (21.6 g, 62.1 mmol), and benzoic acid (0.3 g) were added at room temperature. The resulting reaction mixture was refluxed at °C for 18 h until TLC showed complete conversion of the starting material. The reaction mixture was allowed to come to room temperature and concentrated under reduced pressure to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh, hexane/ethyl acetate, 80/10] to obtain the title compound **7** (9.0 g, 89.0%) as analytically pure low melting solid. R_f 0.5 (30%EtOAc/hexane); $[\alpha]_D^{28}$ −139 (*c* 1.1, $CHCl_3$); IR (KBr, neat): 1049, 1163, 1216, 1372, 1720, 2932, 2985, 3483; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (3H, t, *J*=7.16 Hz, *CH*$_3$CH$_2$), 1.38 (3H, s, CH_3), 1.51 (3H, s, CH_3), 4.11–4.24 (4H, m, 2× CH_2), 4.29–4.36 (1H, m, CH), 4.74–4.81 (1H, m, CH), 6.08 (1H, dd, *J*=1.51, 15.48 Hz, CH), 6.86 (1H, dd, *J*=5.66, 15.86 Hz, CH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.2, 25.2, 27.6, 60.6, 61.8, 75.9, 78.2, 109.5, 123.0, 142.0, 165.8. MS (ESI): *m*/*z* 253 $(M+Na)^+$. HRMS: calcd for $C_8H_{14}O_5Na$: 253.10464. Found 253.10406.

*4.1.4. Ethyl 3-((4R,5S)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propanoate (**8**).* To a stirred solution of conjugated alkene **7** (8.2 g, 35.6 mmol) in MeOH (100 mL), $NiCl_4 \cdot 6H_2O$ (1.7 g, 7.13 mmol) was added at 0 °C. The resulting mixture was stirred at 0 °C for 10 min and $NaBH_4$ (2.7 g, 71.3 mmol) was added in small portions. The reaction mixture was stirred for another 3 h and quenched with water. The whole reaction mixture was concentrated to get the residue, which was extracted with EtOAc. The organic extract was washed with brine and dried over anhydrous Na_2SO_4, and evaporated. The crude reaction mixture was purified by silica gel column chromatography using EtOAc/hexane (25%) as an eluent to provide the corresponding saturated ester compound **8** (7.8 g, 94.9%) as a clear oil. R_f 0.5 (50% EtOAc/hexane); $[\alpha]_D^{28}$ +21.3 (*c* 2.1, $CHCl_3$); IR (KBr, neat): 1041, 1163, 1250, 1372, 1732, 2934, 2985, 3472; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (3H, t, *J*=7.17 Hz, *CH*$_3$CH$_2$), 1.32 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.77–1.85 (2H, m, CH_2), 2.31–2.55 (2H, m, CH_2), 3.60–3.63 (2H, m, *CH*$_2$OH), 4.08–4.17 (4H, m, 2CH, *CH*$_2$CH$_3$); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.1, 24.5, 25.3, 28.0, 31.0, 60.4, 61.4, 75.9, 77.7, 108.2, 173.1; MS (ESI): *m*/*z* 255 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 255.12029. Found 255.12007.

*4.1.5. Ethyl 3-((4R,5R)-5-formyl-2,2-dimethyl-1,3-dioxolan-4-yl) propanoate (**9**).* To a stirred solution of IBX (4.1 g, 15.0 mmol) in dry DMSO (10 mL), a solution of compound **8** (2.5 g, 10.7 mmol) in THF (60 mL) was added drop wise at room temperature. The resulting reaction mixture was stirred for 3 h until TLC showed complete conversion of the starting material. The reaction mixture was quenched by addition of cold water (15 mL) and diluted with diethyl ether (50 mL). Organic layer was separated and washed with satd $NaHCO_3$ (2×10 mL), dried (Na_2SO_4), and concentrated under reduced pressure to obtain the title compound **9** (2.28 g, 92.3%) as a thick syrup, which was used further without purification. R_f 0.8 (50% EtOAc/hexane); IR (KBr, neat): 1074, 1272, 1373, 1454, 1732, 2931; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (3H, t, *J*=7.32 Hz, CH_3), 1.40 (3H, s, CH_3), 1.57 (3H, s, CH_3), 1.99–2.13 (2H, m, CH_2), 2.39–2.55 (2H, m, CH_2), 4.14 (2H, q, *J*=7.32, 14.64 Hz, *CH*$_2$CH$_3$), 4.29–4.33 (1H, m, CH), 4.36–4.41 (1H, m, CH), 9.67 (1H, d, *J*=2.44 Hz, CHO); ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.1, 19.1, 25.2, 27.6, 30.9, 60.5, 71.7, 81.7, 110.6, 172.5, 201.8. MS (ESI): *m*/*z* 253 $(M+Na)^+$. HRMS: calcd for $C_8H_{14}O_5Na$: 253.10464. Found 253.10493.

*4.1.6. Methyl 3-((4R,5S)-5-ethynyl-2,2-dimethyl-1,3-dioxolan-4-yl) propanoate (**10**).* To a stirred solution of K_2CO_3 (2.4 g, 17.4 mmol) and dimethyl-1-diazo-2-oxopropylphosphonate (1.8 g, 9.56 mmol) in dry MeOH (15 mL), aldehyde **9** (2.0 g, 8.7 mmol) dissolved in dry MeOH (5 mL) was added drop wise at room temperature. The resulting mixture was stirred for 4 h until TLC showed complete conversion of the starting material. The reaction mixture was filtered to remove inorganic solid, and the filtrate was concentrated under reduced pressure to obtain alkyne compound **10** (1.38 g, 75.0%) as pale yellow oil. R_f 0.7 (30% EtOAc/hexane); $[\alpha]_D^{28}$ −17.1 (*c* 1.1, $CHCl_3$); IR (KBr, neat): 863, 1064, 1226, 1371, 1738, 2934, 2987, 3272; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, s, CH_3), 1.52 (3H, s, CH_3), 2.01–2.13 (2H, m, CH_2), 2.45–2.54 (3H, m, CH_2, CH), 3.69 (3H, s, CH_3), 4.10–4.17 (1H, m, CH), 4.77 (1H, dd, *J*=*2.26*, *5.66* Hz, CH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 25.8, 26.2, 27.6, 30.3, 51.6, 68.7, 76.0, 76.5, 79.4, 109.8, 173.4; MS (ESI): *m*/*z* 235 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 235.09408. Found 235.09374.

*4.1.7. Methyl-3-((4R,5S)-2,2-dimethyl-5-((E)-pent-3-en-1-ynyl)-1,3-dioxolan-4-yl)propanoate (**11**).* To a stirred solution of $Pd(PPh_3)_2Cl_2$ (264 mg, 0.377 mmol) and CuI (229 mg, 1.20 mmol) in piperidine

were added solutions of *trans*-1-bromopropene (958 mg, 7.92 mmol) in piperidine and acetylene compound **10** (800 mg, 3.77 mmol) in DMF under argon atmosphere. The resultant mixture was stirred for 10 min at room temperature and then heated to 70 °C for 5 h. The reaction mixture was filtered through Celite and filtrate was concentrated under reduced pressure to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh, hexane/ethyl acetate, 80/10] to obtain the title compound **11** (670 mg, 70.5%) as a pale yellow liquid. R_f 0.5 (10% EtOAc/hexane); $[\alpha]_D^{28}$ −21.1 (*c* 1.0, $CHCl_3$); IR (KBr, neat): 1072, 1166, 1225, 1370, 1738, 2930; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (3H, s, CH_3), 1.51 (3H, s, CH_3), 1.78 (3H, d, *J*=6.99 Hz, CH_3), 1.99–2.07 (2H, m, CH_2), 2.42–2.55 (2H,m, CH_2), 3.68 (3H, s, CH_3), 4.08–4.16 (1H, m, CH), 4.88 (1H, d, *J*=4.99 Hz, CH), 5.51 (1H, d, *J*=15.99 Hz, CH), 6.14–6.22 (1H, m, CH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 18.6, 25.9, 26.5, 27.8, 30.3, 51.6, 69.4, 76.9, 82.5, 86.6, 109.4, 109.9, 140.7, 173.5; MS (ESI): *m*/*z* 275 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 275.12538. Found 275.12516.

*4.1.8. Methyl-3-((4R,5S)-2,2-dimethyl-5-((1Z,3E)-penta-1,3-dienyl-1)-1,3-dioxolan-4-yl) propanoate (**12**).* To a suspension of activated Zn (1.25 g), alkyne **11** (500 mg, 1.98 mmol) in MeOH (20 mL) was added drop wise at room temperature. The resulting reaction mixture was heated for 60 °C and stirred for 12 h until the TLC showed complete conversion of the starting material. The reaction mixture was filtered to remove the inorganic solid, and filtrate was concentrated under reduced pressure and diluted with ethyl acetate (15 mL). The organic layer was washed with water and dried over Na_2SO_4, and concentrated under reduced pressure to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh, hexane/ethyl acetate, 80/10] to obtain the title compound **12** (377 mg, 74.9%) as a light yellow liquid. R_f 0.6 (EtOAc/hexane, 20/80); $[\alpha]_D^{28}$ +17.6 (*c* 1.0, $CHCl_3$); IR (KBr, neat): 1071, 1164, 1273, 1378, 1736, 2925; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.79 (3H, dd, *J*=1.13, 6.79 Hz, CH_3), 1.99–2.12 (2H, m, CH_2), 2.28–2.54 (2H, m, CH_2), 3.67 (3H, s, CH_3), 4.12–4.20 (1H, m, CH), 5.05 (1H, dd, *J*=5.28, 8.67 Hz, CH), 5.30 (1H, t, *J*=9.44, 10.57 Hz, CH), 5.73–5.80 (1H, m, CH), 6.15 (1H, t, *J*=10.57, 11.33 Hz, CH), 6.30 (1H, t, *J*=12.46, 15.48 Hz, CH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 19.1, 25.6, 26.0, 27.6, 28.2, 51.5, 71.7, 74.1, 108.1, 123.3, 126.0, 128.7, 130.8, 173.7; MS (ESI): *m*/*z* 277 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 277.14103. Found 277.14066.

*4.1.9. (R)-5-((S,2Z,4E)-1-Hydroxyhexa-2,4-dienyl)dihydrofuran-2(3H)-one (**1**).* To a stirred solution of ester **12** (210 mg, 0.826 mmol) in THF (25 mL), catalytic amount of concd HCl was added at 0 °C. And the resulting reaction mixture was stirred at room temperature for 12 h, until the TLC showed complete conversion of the starting material. The reaction mixture was neutralized by addition of solid $NaHCO_3$ and filtered to remove inorganic solid. The filtrate was concentrated under reduced pressure to obtain a residue, which was chromatographed [SiO_2, 60–120 mesh, hexane/ethyl acetate, 80/10] to obtain the title compound **1** (118 mg, 78.6%) as a colorless oil. R_f 0.3 (EtOAc/hexane, 50/50); $[\alpha]_D^{28}$ +66.1 (*c* 1.1, $CHCl_3$), [lit.[2] $[\alpha]_D^{28}$ +65.2 (*c* 1.3, $CHCl_3$)]; IR (KBr, neat): 1054, 1469, 1621, 1713, 2922, 3435; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (3H, ddd, *J*=1.51, 3.06, 6.79 Hz, CH_3), 2.13–2.38 (2H, m, CH_2), 2.45–2.70 (2H, m, CH_2), 4.54 (1H, dt, *J*=3.02, 6.79, 10.57 Hz, CH), 4.89 (1H, dd, *J*=2.26, 8.68 Hz, CH), 5.21 (1H, t, *J*=7.93 Hz, CH), 5.78–5.90 (1H, m, CH), 6.12–6.35 (2H, m, 2× CH); ^{13}C NMR (300 MHz, $CDCl_3$): δ 18.3, 21.2, 28.5, 68.4, 82.3, 123.8, 126.0, 132.9, 133.6, 177.5; MS (ESI): *m*/*z* 205 $(M+Na)^+$; HRMS: calcd for $C_8H_{14}O_5Na$: 205.08357. Found 205.08383.

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Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra for all new compounds.

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.05.012.

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