Synthesis of spirocyclopente-dione anthracene adduct, precursor of the cyclopentenone prostaglandins via ring-closing metathesis reaction

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Cross-conjugated, Dienone, Ring closing metathesis, Cyclopentenones, CMMB

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Synthesis of Spirocyclopente-Dione Anthracene Adduct, Precursor of the Cyclopentenone Prostaglandins Via Ring-Closing Metathesis Reaction

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\textbf{Abstract:} A synthesis of the spirocyclopente-dione anthracene adduct, a precursor of the cyclopentenone prostaglandins has been reported. The synthesis involved a Diels-Alder reaction of anthracene and dimethyl fumarate to afford followed by reduction, oxidation and esterification reactions to provide methyl ester anthracene adduct, which further converted to the allylic alcohol. Then, Ring-Closing Metathesis (RCM) reaction afforded the cyclopentenol anthracene adduct, which after oxidation provided the spirocyclopente-dione anthracene adduct in good yields.

\textbf{Keywords:} Cross-conjugated, Dienone, Ring closing metathesis, Cyclopentenones

\section*{Introduction}

Functionalized cyclopentenones are considered important precursors in the synthesis of a large number of bioactive natural products such as conjugated dienone prostanoids, clavulone I, clavulone II\textsuperscript{1-2} and claviridic acids A-E\textsuperscript{3}, all exhibiting strong cytotoxicity and anticancer activity. Several synthetic approaches have been proposed to prepare this class of compounds including the Nazarov cyclisation\textsuperscript{4}, [3+2] annulations\textsuperscript{5}, metal-catalysed cyclisations\textsuperscript{6} and Diels-Alder/retro Diels-Alder reactions using anthracene\textsuperscript{7}. In our previous research of stereoselective synthesized cyclopentenone\textsuperscript{8}, we found the use of sterically crowded anthracene moiety leads to stereocntrol and asymmetric transformations and subsequent retro-Diels-Alder reactions using anthracene. In our previous research of stereoselective synthesized cyclopentenone\textsuperscript{8}, we found the use of sterically crowded anthracene moiety leads to stereocntrol and asymmetric transformations and subsequent retro-Diels-Alder reactions using anthracene\textsuperscript{7}. In our previous research of stereoselective synthesized cyclopentenone\textsuperscript{8}, we found the use of sterically crowded anthracene moiety leads to stereocntrol and asymmetric transformations and subsequent retro-Diels-Alder reactions using anthracene\textsuperscript{7}. However, the cyclization process using \(\beta\)-allyl ester with an excess of LDA provided cyclopentenone in moderate yields together with the formation of the enaminone\textsuperscript{10}. As an extension, we here report a
novel building block for the synthesis of cyclopentenone prostaglandins, in the particular PGA₁ analog clavulones. The synthesis of this key compound, spirocyclopentadiene anthracene adduct, could be envisioned from the cyclopentenol readily obtained from the 1,6-diene using a ring-closing metathesis reaction.

Figure 1

Experimental

Melting points were determined on a Stuart Scientific SMP 2 melting point apparatus and are uncorrected. Infrared spectra were recorded as CH₂Cl₂-films with a Perkin Elmer Spectrum GX FT-IR spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded in (D) chloroform solutions at 300 MHz for ¹H and 75 MHz for ¹³C with a Bruker AVANCE 300 spectrometer. Tetramethysilane was used as the internal standard. Mass spectra were recorded on a Polaris Q or Hewlett Packard 5973 mass spectrometer.

9,10-Dihydro-9,10-ethanoanthracene-11,12-dimethyl ester (3)

A mixture of anthracene (2.00 g, 11.22 mmol), dimethyl fumarate (2.05 g, 14.23 mmol) and xylene (15 mL) in a pressured tube with boiling chips was heated at 120 °C for 48 h. The reaction mixture was cooled to room temperature and the xylene was subsequently removed under vacuum. The crude product was purified using column chromatography (silica gel, 30:1 hexane/EtOAc) to afford the adduct 3 (2.82 g, 78%) as a white solid, m.p. 103-105 °C (lit. 107-108 °C); IR (CH₂Cl₂) νmax: 1732, 1459, 1435, 1221, 1198, 1018, 760 cm⁻¹; ¹H NMR δ 7.28-7.31 (m, 2H, ArH), 7.22-7.25 (m, 2H), 7.07-7.14 (m, 4H), 4.73 (s, 2H), 3.62 (s, 6H), 3.42 (s, 2H); ¹³C NMR δ 172.8, 142.0, 140.3, 126.4, 126.3, 124.6, 123.8, 52.2, 47.8, 46.7.

9,10-Dihydro-9,10-ethanoanthracene-11,12-dimethyl alcohol (4)

To a solution of 3 (2.75 g, 8.54 mmol) in THF (60 mL) at 0 °C lithium aluminium hydride (1.94 g, 51.2 mmol) was slowly added. The mixture was stirred at 0 °C under argon atmosphere for 30 min. The reaction mixture was quenched with sat. NaHCO₃ solution and extracted with Et₂O (3×30 mL). The combined organic phase was dried (Na₂SO₄), filtered and concentrated under reduced pressure to give the diol 4 (2.15 g, 98%) as a white solid; m.p. 196-198 °C; IR (CH₂Cl₂) νmax: 3442, 3054, 2987, 1422, 1022 cm⁻¹; ¹H NMR δ 7.38-7.35 (m, 4H), 7.18-7.15 (m, 4H), 4.44 (s, 2H), 3.22-3.17 (m, 2H), 2.89-2.81 (m, 2H), 1.38-1.33 (m, 2H); ¹³C NMR δ 144.5, 141.7, 126.1, 125.8, 123.4, 64.5, 45.9, 45.3; HRESI-MS m/z calcd for [M+Na]+ C₁₈H₁₈NaO₂: 289.1193, found: 289.1182.

9,10-Dihydro-9,10-ethanoanthracene-11-acetoxy-12-methanol (5)

To a solution of the diol 4 (5.80 g, 21.8 mmol) in DMF (8 mL) at room temperature pyridine (2.11 mL, 26.2 mmol) was added followed by acetic anhydride (2.06 mL, 21.8 mmol). The mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with water and extracted with CH₂Cl₂ (2×20 mL). The combined extracts were dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 3:1 hexane/EtOAc) to give the mono-acetate 5 (3.48 g, 52%) as a white solid; m.p. 89-91 °C; IR (CH₂Cl₂) νmax: 3451, 3054, 2987, 1736, 1422, 1025 cm⁻¹; ¹H NMR δ 7.27-7.23 (m, 4H), 7.11-7.07 (m, 4H), 4.32 (d, J = 1.8 Hz, 1H), 4.21 (d, J = 1.8 Hz, 1H), 3.81 (dd, J = 10.6,
5.8 Hz, 1H), 3.51 (dd, \(J = 10.4, 8.7\) Hz, 1H), 3.27 (dd, \(J = 10.6, 5.8\) Hz, 1H), 3.06 (dd, \(J = 10.4, 8.7\) Hz, 1H), 2.48 (br. s, 1H), 2.03 (s, 3H), 1.66-1.52 (m, 2H); 13C NMR \(\delta = 171.2, 143.5, 143.1, 140.7, 140.4, 126.3, 126.2, 125.9, 125.8, 125.4, 123.5*2, 67.1, 65.5, 45.9, 45.7, 45.5, 42.2, 21.0;\) HRESI-MS \(m/z\) cald for [M+Na]+ C20H20NaO3: 331.1310, found: 331.1306.

**9,10-Dihydro-9,10-ethanoanthracene-11-acetoxy-12-acetic acid (6)**

A solution of alcohol 5 (0.22 g, 0.71 mmol) in acetone (6 mL) was treated with Jones reagent\(^{18}\) (4 mL) at 0 °C until TLC analysis showed the reaction was complete (ca. 1 h). Isopropanol (0.6 mL) was added slowly drop wise to destroy excess reagent and the mixture was stirred for another 5-10 min until the colour of the solution changed from red to green. CH2Cl2 (20 mL) and water (20 mL) were added. The aqueous phase was extracted with CH2Cl2 (10 mL \(\times 3\)). The combined organic extracts were washed with water (40 mL) and brine (40 mL) and then dried (Na2SO4), filtered and evaporated in vacuo to give compound 6 (0.21 g, 91%) as a yellow oil; IR (CH2Cl2) \(\nu_{\text{max}}: 3436, 2987, 1737, 1708, 1422, 1036 \text{ cm}^{-1};\) 1H NMR \(\delta = 7.35-7.28 (m, 4H), 7.18-7.12 (m, 4H), 4.68 (d, \(J = 2.1\) Hz, 1H), 4.33 (d, \(J = 2.1\) Hz, 1H), 3.89-3.84 (m, 1H), 3.77-3.70 (m, 1H), 2.73-2.65 (m, 1H), 2.42 (dd, \(J = 5.6, 2.3\) Hz, 1H), 2.60 (s, 3H); 13C NMR \(\delta = 178.1, 171.0, 143.3, 141.9, 140.2, 139.9, 126.4*3, 126.1, 125.5, 125.3, 123.6, 123.5, 66.7, 48.2, 46.3, 45.9, 41.7, 20.9;\) HRESI-MS \(m/z\) cald for [M+Na]+ C20H18NaO4: 345.1103, found: 345.1089.

**9,10-Dihydro-9,10-ethanoanthracene-11-methanol-12-methyl ester (7)**

To a solution of 6 (2.34 g, 7.27 mmol) in methanol (14 mL) was added drop wise conc. H2SO4 (1 mL). The mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with water and extracted with CH2Cl2 (3 \(\times 20\) mL). The combined extracts were dried (Na2SO4), filtered and concentrated to give 7 (1.82 g, 85%) as a yellow oil; IR (CH2Cl2) \(\nu_{\text{max}}: 3443, 2987, 1733, 1422, 1023 \text{ cm}^{-1};\) 1H NMR \(\delta = 9.20 (\text{br. s, 1H}), 7.32-7.23 (m, 4H), 7.11-7.05 (m, 4H), 4.62 (d, \(J = 2.1\) Hz, 1H), 4.31 (d, \(J = 2.1\) Hz, 1H), 3.27 (s, 3H) 3.09-2.96 (m, 2H), 2.58-2.50 (m, 1H); 13C NMR \(\delta = 177.2, 143.6, 142.4, 140.7, 140.2, 126.3, 126.28, 126.25, 126.0, 125.6, 125.5, 125.3, 123.6, 123.5, 75.8, 58.9, 48.7, 46.1, 45.6, 42.7;\) HRESI-MS \(m/z\) cald for [M+Na]+ C19H18NaO3: 317.1154, found: 317.1148.

**11-(tert-Butyl-dimethyl-silanyloxy)methyl-9,10-dihydro-9,10-ethanoanthracene-12-methyl ester (8)**

To a solution of alcohol 7 (1.50 g, 5.09 mmol) in dry CH2Cl2 (43 mL) under an argon atmosphere imidazole (0.66 g, 10.2 mmol) was added followed by TBDMSCl (0.88 g, 5.61 mmol). The mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with sat. NaHCO3 solution and extracted with CH2Cl2 (2 \(\times 30\) mL). The combined extracts were dried (Na2SO4), filtered and concentrated. Purification by flash column chromatography (silica gel, 30:1 hexane/ EtOAc) gave silyl ether 8 (1.68 g, 81%) as a white solid, m.p. 81.7-84.8 °C; IR (CH2Cl2) \(\nu_{\text{max}}: 3445, 2953, 1737, 1470, 1253, 1094, 837, 746 \text{ cm}^{-1};\) 1H NMR \(\delta = 7.21-7.13 (m, 4H), 7.03-6.98 (m, 4H), 4.48 (d, \(J = 2.3\) Hz, 1H), 4.30 (d, \(J = 2.3\) Hz, 1H), 3.20 (s, 3H, OCH3), 3.12-3.07 (m, 1H), 2.64 (d, \(J = 9.1\) Hz, 1H), 2.58-2.52 (m, 1H), 2.06-2.04 (m, 1H), 0.80 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); 13C NMR \(\delta = 173.5, 144.1, 142.6, 141.1, 140.8, 126.4, 126.2*2, 125.9, 125.8, 125.1, 123.6, 123.5, 65.7, 61.9, 48.0, 46.9, 45.7, 45.6, 26.1;\) HRESI-MS \(m/z\) cald for [M+Na]+ C25H32NaO3Si: 431.1154, found: 431.1148.

**11-(tert-Butyl-dimethyl-silanyloxy)methanol-9,10-dihydro-9,10-ethanoanthracene-12,12-dimethylester (9)**

To a solution of 2 M lithium diisopropylamide (0.74 mL, 1.47 mmol) in dry THF (2.5 mL) at -78 °C under argon atmosphere a solution of ester 8 (0.50 g, 1.22 mmol) was added in dry
THF (5 mL) and the mixture was allowed to warm to 0 °C for 2 h. Methyl cyanoformate (0.12 mL, 1.47 mmol) was added at -78 °C and the mixture stirred at 0 °C for 2 h. The resulting mixture was quenched with an aqueous saturated NaHCO₃ (20 mL) and extracted with CH₂Cl₂ (2×15 mL) which was washed with water (20 mL) and saturated NaCl (20 mL). The combined extracts were dried (Na₂SO₄), filtered and concentrated in vacuo. Purification of the residue by flash column chromatography (silica gel, 25:1 hexane/ EtOAc) gave 9 (0.41 g, 81%) as a white solid, m.p. 129-131 °C; IR (CH₂Cl₂) ν max: 2952, 1741, 1459, 1220, 1095, 837 cm⁻¹; ¹H NMR δ 7.44 (d, J = 7.3 Hz, 1H), 7.30 (d, J = 7.3 Hz, 2H), 7.23 (d, J = 7.1 Hz, 1H), 7.14 (d, J = 7.3 Hz, 1H), 7.04 (dd, J = 7.5, 7.3 Hz, 1H), 4.8 (s, 1H), 4.58 (d, J = 2.4 Hz, 1H), 3.57 (s, 3H), 3.55 (s, 3H), 3.54-3.51 (m, 1H), 3.30-3.22 (m, 1H), 2.67 (dd, J = 10.8, 9.5 Hz, 1H), 0.93 (s, 9H), 0.00 (s, 6H). ¹³C NMR δ 170.7, 170.1, 143.9, 141.6, 140.5, 140.1, 127.0, 126.9, 126.1, 126.0, 125.9, 125.3, 124.5, 124.4, 62.4, 61.9, 53.1, 52.3, 51.0, 47.1, 45.6, 26.2, -5.16, -5.2. HRESI-MS m/z cald for [M-H]- C₂₇H₃₃O₅Si: 465.2097, found: 465.2118.

11-(tert-Butyl-dimethyl-silanyloxy)methanol-9,10-dihydro-9,10-ethanoanthracene-12,12-dimethanol (10)

To adduct 9 (0.16 g, 0.33 mmol) in Et₂O (2 mL) at 0 °C lithium aluminium hydride (53 mg, 1.4 mmol) was slowly added. The mixture was stirred at 0 °C under argon atmosphere for 30 min. The reaction was quenched with saturated NaHCO₃ solution and extracted with Et₂O (3×30 mL). The combined extracts were dried (Na₂SO₄), filtered and concentrated under reduced pressure to give a diol 10 (74 mg, 61%) as a white solid, m.p. 204-206 °C; IR (CH₂Cl₂) ν max: 3262, 2929, 1466, 1253, 1059, 835 cm⁻¹; ¹H NMR δ 7.37-7.34 (m, 1H), 7.28-7.19 (m, 3H), 7.13-7.08 (m, 4H), 4.35 (s, 1H), 4.06 (d, J = 1.78 Hz, 1H), 3.47 (dd, J = 10.8, 5.2 Hz, 2H), 3.47 (dd, J = 10.6, 1.6 Hz, 1H), 3.35-3.32 (m, 3H), 2.96 (dd, J = 10.7, 10.3 Hz, 1H), 2.65 (br.s, 1H), 1.52 (qd, J = 5.1, 1.9 Hz, 1H), 0.86 (s, 9H), 0.066 (s, 3H), 0.044 (s, 3H). ¹³C NMR δ 143.6, 141.8, 141.4, 140.9, 126.3, 126.2*2, 126.0, 125.8, 125.3, 124.9, 123.2, 68.2, 65.3, 65.2, 49.4, 48.5, 48.1, 47.9, 26.0, -5.13, -5.29. HRCl-MS m/z cald for [M+H]+C₂₅H₃₅O₃Si: 411.2355, found: 411.2361.

11-((tert-Butyl-dimethyl-silanyloxy)methanol-9,10-dihydro-9,10-ethanoanthracene-12,12-diyl)bis(prop-2-en-1-ol) (12)

Vinyl magnesium bromide (1.9 mL, 1.91 mmol) was added drop wise to the solution of the aldehyde 11 (0.15 g, 0.38 mmol) in dry Et₂O (5 mL) at -78 °C under argon atmosphere. The mixture was stirred at -78 °C for 40 min. The reaction was quenched with sat.NH₄Cl.
at -78 °C and allowed to warm to room temperature. The mixture was extracted with Et₂O (2×20 mL). The combined organic layers were washed with brine, dried over anhyd. Na₂SO₄, filtered and concentrated. Purification of the residue by flash column chromatography (silica gel, 20:1 hexane/EtOAc) gave **12** (16 mg g, 8.9%) as a yellow oil; IR (CH₂Cl₂) ν max: 3350, 2929, 1469, 1254, 1086, 836 cm⁻¹; ¹H NMR δ ¹H ; 7.36-7.34 (m, 1H), 7.25-7.22 (m, 2H), 7.10-7.07 (m, 5H), 6.33-6.26 (m, 2H), 6.24-6.18 (m, 2H), 5.22 (dd, J = 17.1, 10.4 Hz, 2H), 5.06 (dd, J = 17.1, 10.4 Hz, 2H), 4.71 (s, 1H), 4.29 (d, J = 1.5 Hz, 1H), 3.79 (d, J = 6.5 Hz, 1H), 3.69-3.65 (dd, J = 10.7, 7.6 Hz, 1H), 3.50 (dd, J = 10.8, 6.9 Hz, 1H), 3.32 (d, J = 5.0 Hz, 1H), 1.97 (t, J = 7.2 Hz, 1H), 0.92 (s, 9H), 0.096 (s, 3H), 0.065 (s, 3H). ¹³C NMR δ 143.9, 142.1, 141.9, 141.8, 139.5, 139.4, 126.3, 126.1, 126.0, 125.9, 125.84, 125.82, 125.1, 123.4, 117.1, 114.9, 80.5, 76.9, 65.2, 53.9, 49.3, 48.3, 48.26, 26.1, -5.1, -5.2. HRESI-MS m/z cald for [M] C₂₉H₃₈O₃Si: 462.2590, found: 462.2613.

**11-((tert-Butyl-dimethyl-silanyloxy)methanol-9,10-dihydrospiro-[9,10-ethanoanthracene -12,1'-cyclopen[3]ene]-2',5'-diol (13)**

To a solution of compound **12** (0.11 g, 0.25 mmol) Grubb I catalyst (10 mg, 0.012 mmol) in CH₂Cl₂ (4.3 mL) was added. The reaction was heated at 40 °C under argon atmosphere for 15 h and then concentrated under reduced pressure. The crude product was purified by Flash column chromatography (silica gel, 6:1 hexane/EtOAc) to give compound **13** (56 mg, 53%) as a yellow oil; IR (CH₂Cl₂) ν max: 2962, 1704, 1463, 1260 cm⁻¹; ¹H NMR δ ¹H ; 7.33(d, J = 7.2 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.26 (s, 1H), 7.20-7.08 (m, 7H), 4.17 (s, 1H), 3.60 (dd, J = 9.8, 5.6 Hz, 1H), 3.24 (dd, J = 10.8, 9.8 Hz, 1H), 2.55 (dd, J = 10.8, 5.6 Hz, 1H), 0.69 (s, 9H), -0.13 (s, 3H), -0.17 (s, 3H). ¹³C NMR δ 204.4, 201.2, 148.8, 145.4, 144.6, 141.4, 140.1, 138.9, 126.8, 126.6, 126.1, 126.0, 125.7, 125.5, 124.8, 123.0, 63.3, 55.2, 51.5, 51.1, 46.5, 25.8, -5.5, -5.6. HRESI-MS m/z cald for [M-H] C₂₇H₃₃O₃Si: 433.2199, found: 433.2174.

**Results and Discussion**

Synthesis of cyclopentenone adduct began from Diels-Alder reaction between the know dimethyl fumarate and anthracene in xylene at 120 °C for 48 h in a sealed tube gave ester **3** in 78% yield (Scheme 1). Reduction of the adduct **3** using LiAlH₄ led to the alcohol **4** in quantitative yield. The di-alcohol **4** was protected as its monoacetate adduct **5** and transformed another alcohol group into carboxylic acid **6** by using Jone reagent as high as 91% yield (Scheme 2). Esterification of the carboxylic acid **6** with methanol in the present of
H$_2$SO$_4$ into their methyl ester was however, obtained the alcohol 7 as the acetate protecting group was cleaved during this reaction. Thus, re-protected the –OH group of the resulting methyl ester 7 with $t$-butyldimethylsilyl chloride gave silyl adduct 8 in 81%.

Scheme 1. Synthetic route to methyl ester adduct 8

Spirocyclopenten-dione 14 required for this synthesis was prepared in a six-steps synthetic route starting with treatment of ester 8 with LDA in THF at -78 °C in the presence of methyl cyanoformate to form dimethyl ester adduct 9 in 81% yield. This was reacted with LiAlH$_4$ in THF at 0 °C forming the primary alcohol 10 (61%), which was further oxidized to the corresponding dialdehyde 11 by Dess-Martin periodinane, both steps proceeding in excellent yield. Compound 11 was then obtained by addition vinylmagnesium bromide to give secondary alcohol 12 (8.9%) as a mixture of four diastereomer, followed by olefin cross metathesis using Grubb’s catalyst to give alkene 13 (53%). Oxidation of di-alcohol 13 with Dess-Martin periodinane gave spirocyclopenten-dione 14 in 93% yield (Scheme 2).

Scheme 2. Synthetic route to Spirocyclopenten-dione 14
Conclusion

The spirocyclopenten-dione anthracene adduct (14), a precursor of the cyclopentenone prostaglandins, has been synthesized in 12 steps. This compound may in the future as a building block to provide an efficient route for the synthesis of prostanoid natural products.

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