Total Synthesis of Leiocarpin C and (+)-Goniodiol via an Olefin Cross-Metathesis Protocol

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A stereoselective total synthesis of leiocarpin C (2) and (+)-Goniodiol (1) by applying olefin crossmetathesis and substrate directed dihydroxylation as the key steps is reported (*Scheme 3*).

Introduction. – Leiocarpin C (**1**) is a natural styryl lactone. Styryl lactones are natural products that exhibit significant biological activities such as antitumor, antifungal, and antibiotic properties [1]. Compound **1** was isolated from the stem bark of the tropical plant *Goniothalamus leiocarpus* [2]. Recently, two syntheses of **1** were reported [3]. (+)-Goniodiol (**2**) was isolated from the stem bark of *Goniothalamus gigantus*, and from the leaves and twigs of *Goniothalamus sesquipedalis* [4b], and it has been shown as selectively cytotoxic against human lung carcinoma cells A-549 (ED_{50} 0.12 µg/ml⁻¹) and p-388 murine leukemia cells (IC_{50} 4.56 µg ml⁻¹) [4]. Several syntheses of **2** have been already reported [3][5]. Impressed by the bio-profile of these compounds, coupled with our interest in the synthesis of such pyrone containing natural products [6], we embarked on their total synthesis. Here, we report the total synthesis of **1** and **2** by a novel methodology involving olefin cross-metathesis and dihydroxylation as the key steps to access the basic premise of the skeleton and thence its elaboration to the targets.



Retrosynthetically (*Scheme 1*), **2** could be obtained from **1** according to a reported procedure [3b]. The latter could be obtained by the desilylation/concomitant lactonization of acyclic ester **3**, which, in turn, could be prepared by the substrate-controlled dihydroxylation of the cross-metathesis product **4**. Formation of **4** could be realized from the cross-metathesis reaction of two olefinic fragments **5** and **6**. While, fragment **5** could be prepared from the known compound **7** [7a] by protection of the secondary alcohol, oxidation of the primary alcohol, and esterification of the

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Scheme 1. Retrosynthethic Analysis



corresponding acid as the key steps, the other fragment **6** could be prepared by the $(t-Bu)Me_2Si$ (TBS) etherification of the known (S)-1-phenylprop-2-en-1-ol ((S)-**8**) that has been earlier prepared by us [7b].

Results and Discussion. – The synthesis of **1** commenced by accessing the two fragments **5** and **6** independently. First, olefinic ester **5** was synthesized as depicted in *Scheme 2*. The secondary OH group of diol **7** was protected as its TBS ether. To differentiate between the primary and secondary alcohols, a selective deprotection of the bis-TBS ether in the primary position was employed: the bis-TBS ether **9** was formed, followed by the selective removal of the primary silyl group to afford **10** (74%). The primary alcohol **10** was oxidized to the corresponding aldehyde under *Swern* oxidation conditions, which was further oxidized [8] to the acid **11** (86% over two steps). The latter was subsequently esterified to afford **5** (85%) using CH₂N₂ in Et₂O.

Scheme 2. Synthesis of Fragment 5



a) (*t*-Bu)Me₂SiCl (TBSCl), 1*H*-imidazole, CH₂Cl₂, 0°, 2 h; 95%. *b*) TsOH, MeOH, -10°, 0.5 h; 74%. *c*) 1. DMSO, (COCl)₂, Et₃N, CH₂Cl₂, -78°, 1 h; 2. NaClO₂, NaH₂PO₄, 2-methylbut-2-ene, H₂O, 0°, 3 h; 86% (overe two steps). *d*) CH₂N₂, Et₂O, 0°, 5 min; 85%.

The known methanol derivative 8 was protected (*Scheme 3*) as its silvl ether 6. Based on our earlier results, this protection was warranted to enable a facile cross-metathesis reaction.



a) TBSCl, 1H-imidazole, CH₂Cl₂, 0°, 0.5 h, 80%.

As outlined in *Scheme 4*, the crucial olefin cross-metathesis reaction [9] between olefinic ester **5** and **6** (1:1.5 ratio) using *Grubbs*-II catalyst, **A**, resulted in product **4** (60%) as a single stereoisomer and the homo-dimer **12** (5%) of **5**. Compound **12** was effectively converted to the desired olefin **4** (60%) by using a second cross-metathesis reaction with **6** under the same conditions. Subsequently, **4** was dihydroxylated [10] to give the desired diol **3** as the major isomer (75%) after column chromatography. The minor diastereoisomer was obtained in 18% yield. Diol **3** was treated with *Amberlyst 15* resin in MeCN to furnish **1** (93%). The physical and spectroscopic data of **1** were identical to the reported ones of natural leiocarpin C $[\alpha]_D^{25} = -63.1$ (c = 0.30, CHCl₃) [2][3]. Finally, **1** was converted to **2** according to the known procedure [3b]. The spectroscopic data of **2** were in agreement with those reported in [3][5].



a) *Grubbs*-II (**A**, 10 mol-%), CH₂Cl₂, r.t., 24 h, 60%. *b*) OsO₄, *N*-methylmorpholine *N*-oxide (NMO), acetone/H₂O 4:1, 24 h, 75%. *c*) *Amberlyst 15*, MeCN, r.t., 2 h, 93%. *d*) **6**, *Grubbs*-II (**A**, 10 mol-%), CH₂Cl₂, r.t., 24 h, 60%.

In summary, a stereoselective synthesis of 1 was achieved in ten steps and in 24.5% overall yield by cross-metathesis, followed by dihydroxylation as the key steps to access the advanced intermediate 3 that was endowed with all stereogenic centers and functionalities; and 3 was easily converted to the target compound 1. Further, the synthesis of 2 was also accomplished.

Experimental Part

General. Org. solns. were dried over anh. Na_2SO_4 and concentrated below 40° in vacuo. Column chromatography (CC): silica gel (SiO₂; Acme's, 60–120 mesh). Optical rotations : JASCO DIP 300 digital polarimeter at 25°. IR Spectra: Perkin-Elmer IR-683 spectrophotometer with NaCl optics. ¹H- and ¹³C-NMR: Bruker Avance-300 MHz, and Inova 500 MHz; 7–10 mM solns. in CDCl₃; TMS as internal standard; J values in Hz. MS: Finnigan Mat 1210 double-focusing mass spectrometers operating at a direct inlet system.

(5R)-2,2,3,3,9,9,10,10-Octamethyl-5-(prop-2-en-1-yl)-4,8-dioxa-3,9-disilaundecane (**9**). To a stirred soln. of diol **7** [7a] (0.30 g, 2.5 mmol) in CH₂Cl₂ (3.5 ml), 1*H*-imidazole (0.7 g, 10.3 mmol) was added at 0°, and the mixture was stirred for 5 min, then TBS-Cl (0.85 g, 5.6 mmol) was added, and the stirring was continued for 2 h at r.t. The mixture was diluted with CH₂Cl₂ (4 ml), and the org. layer was washed with H₂O (5 ml), followed by brine (5 ml). The combined org. layers were dried (Na₂SO₄), evaporated *in vacuo*, and purified by CC (SiO₂; 1% AcOEt/hexane) to afford **9** (0.84 g, 95%). Colorless oily liquid. [α]₂₅²⁵ = -60.4 (*c* = 0.8, CHCl₃). IR (neat): 3454, 2954, 2857, 1742, 1638, 1253, 1088, 834, 776. ¹H-NMR (300 MHz, CDCl₃): 6.03 – 5.86 (*m*, 1 H); 5.16 (*dd*, *J* = 1.5, 12.1, 2 H); 4.03 (*quint*, *J* = 6.0, 1 H); 3.81 (*t*, *J* = 6.7, 2 H); 2.47 – 2.27 (*m*, 2 H); 1.83 – 1.71 (*m*, 2 H); 1.05 (*s*, 18 H); 0.21 (*s*, 6 H); 0.19 (*s*, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 135.0; 116.9; 68.7; 59.6; 42.2; 39.7; 26.1 (6 C); 18.1 (2 C); -4.1 (2 C); -5.1 (2 C). ESI-MS: 345 (71, [*M* + H]⁺), 367 (100, [*M* + Na]⁺).

(3R)-3-{[(tert-Butyl)(dimethyl)sily]oxy]hex-5-en-1-ol (10). To a stirred soln. of 9 (0.82 g, 2.38 mmol) in dry MeOH (10 ml), TsOH (0.04 g, 0.17 mmol) was added at -10° , and the mixture was stirred for 0.5 h. The reaction was quenched with 1.5 ml of Et₃N, the solvent was evaporated, the residue was dissolved in AcOEt (2 × 5 ml), and washed with H₂O (6 ml), and brine (6 ml). The combined org. layers were dried (Na₂SO₄), concentrated *in vacuo*, and purified by CC (SiO₂; 10% AcOEt/hexane) to afford 10 (0.40 g, 74%). Syrupy liquid. $[a]_{25}^{25} = -64.4 (c = 0.85, CHCl_3)$. IR (neat): 3380, 2932, 2858, 1740, 1640, 1253, 1068, 835, 774. ¹H-NMR (300 MHz, CDCl₃): 5.82 – 5.67 (*m*, 1 H); 5.06 (*d*, *J* = 4.1, 1 H); 5.01 (*s*, 1 H); 3.99 – 3.91 (*m*, 1 H); 3.83 – 3.72 (*m*, 1 H); 3.70 – 3.61 (*m*, 1 H); 2.28 (*t*, *J* = 6.2, 2 H); 1.82 – 1.72 (*m*, 1 H); 1.67 – 1.56 (*m*, 1 H); 0.89 (*m*, 9 H); 0.09 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 134.4; 117.3; 71.1; 60.0; 41.6; 37.6; 25.7; 17.9; -4.4; -4.8. ESI-MS: 231 (23, $[M + H]^+$), 253 (100, $[M + Na]^+$). HR-MS: 253.1601 (C₁₂H₂₆NaO₂Si⁺; calc. 253.1599).

(3R)-3-{[(tert-Butyl)(dimethyl)silyl]oxy]hex-5-enoic Acid (11). To a soln. of oxalyl chloride (0.28 ml, 2.47 mmol) in dry CH₂Cl₂ (3 ml) at -78° , dry DMSO (0.27 ml, 4.95 mmol) was added dropwise and stirred for 10 min. A soln. of 10 (0.38 g, 1.65 mmol) in dry CH₂Cl₂ (2 ml) was added, and the mixture was stirred for 1 h at -78° . The reaction was quenched with Et₃N (1.28 ml, 9.9 mmol), and the mixture was diluted with CH₂Cl₂ (5 ml), washed with H₂O (4 ml) and brine (4 ml), dried (Na₂SO₄), and evaporated to furnish the corresponding aldehyde. To a cooled (0°) soln. of the above aldehyde (0.38 g, 1.65 mmol) in t-BuOH (2 ml), 2-methylbut-2-ene (1 ml), followed by a soln. of NaClO₂ (0.3 g, 3.3 mmol) and NaH₂PO₄ (0.51 g, 3.3 mmol) in H₂O (1 ml), was added, and the mixture was stirred at r.t. for 3 h. The solvent was evaporated, the residue was dissolved in AcOEt (5 ml) and washed with H₂O (5 ml) and brine (5 ml), and dried (Na₂SO₄). Evaporation of the solvent under reduced pressure and purification of the residue by CC (SiO₂; 12% AcOEt/hexane) gave **11** (0.34 g, 86% over two steps). Yellow syrup. $[\alpha]_{25}^{25} = -48.2$ (c = 0.7, CHCl₃). IR (neat): 3380, 2932, 2858, 1740, 1640, 1253, 1068, 835, 774. ¹H-NMR $(300 \text{ MHz}, \text{CDCl}_3): 5.84 - 5.67 (m, 1 \text{ H}); 5.09 (s, 1 \text{ H}); 5.05 (d, J = 3.5, 1 \text{ H}); 4.18 (quint, J = 5.6, 1 \text{ H});$ 2.51-2.37 (m, 2 H); 2.27 (pseudo-t, J = 6.2, 2 H); 0.86 (s, 9 H); 0.07 (s, 3 H); 0.04 (s, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 177.3; 133.7; 118.0; 68.8; 41.9; 41.7; 25.7; 17.9; -4.5; -4.9. ESI-MS: 245 (26, [M+ H]⁺), 267 (100, $[M + Na]^+$). HR-MS: 267.1405 (C₁₂H₂₄NaO₃Si⁺; calc. 267.1392).

Methyl (3R)-3-{[(tert-*Butyl*)(*dimethyl*)*silyl*]*oxy*]*hex-5-enoate* (**5**). To a stirred soln. of **11** (0.32 g, 1.31 mmol) in Et₂O (5 ml), CH₂N₂ in Et₂O was added, until yellow color sustained at 0°, and the mixture was stirred for 5 min. Evaporation of the solvent under reduced pressure and purification of the residue by CC (SiO₂; 2% AcOEt/hexane) afforded **5** (0.28 g, 85%). Yellow oil. $[\alpha]_{D}^{25} = -68.4$ (c = 0.55, CHCl₃). IR (neat): 3078, 2932, 2858, 1711, 1644, 1433, 1254, 1090, 834, 776. ¹H-NMR (300 MHz, CDCl₃): 5.84–5.68 (m, 1 H); 5.07 (s, 1 H); 5.03–4.99 (m, 1 H); 4.17 (*quint*., J = 6.0, 1 H); 3.64 (s, 3 H); 2.40–2.38 (m, 2 H); 2.27–2.23 (m, 2 H); 0.85 (s, 9 H); 0.06 (s, 3 H); 0.02 (s, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 177.3;

133.7; 118.0; 68.8; 61.5; 41.9; 41.7; 25.6; 17.9; -4.5; -5.01. ESI-MS: 259 (5, $[M + H]^+$), 281 (70, $[M + Na]^+$). HR-MS: 281.1561 (C₁₃H₂₆NaO₃Si⁺; calc. 281.1548).

 $(tert-Butyl)(dimethyl){[(1S)-1-phenylprop-2-en-1-yl]oxy]silane}$ (6). To a stirred soln. of **8** [7b] (0.25 g, 1.86 mmol) in CH₂Cl₂ (3.5 ml), 1*H*-imidazole (0.25 g, 3.67 mmol) was added at 0°, and the mixture was stirred for 5 min; then, TBS-Cl (0.30 g, 2.04 mmol) was added, and the mixture was stirred for 0.5 h at r.t. The mixture was diluted with CH₂Cl₂ (4 ml), and the org. layer was washed with H₂O (5 ml), followed by brine (5 ml). The combined org. layers were dried (Na₂SO₄), evaporated *in vacuo*, and purified by CC (SiO₂; 1% AcOEt/hexane) to afford **6** (0.37 g, 80%). Colorless oil. $[a]_D^{25} = -46.0$ (c = 0.25, CHCl₃). IR (neat): 3450, 2930, 2860, 1710, 1676, 1390, 1219, 830. ¹H-NMR (300 MHz, CDCl₃): 7.38 (d, J = 7.3, 1 H); 7.31–7.17 (m, 4 H); 5.95–5.84 (m, 1 H); 5.27 (td, J = 1.3, 16.9, 1 H); 5.15 (d, J = 5.6, 1 H); 5.04 (td, J = 1.3, 10.1, 1 H); 0.93 (s, 9 H); 0.14 (s, 3 H); 0.08 (s, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 141.6; 128.1; 126.9; 125.9; 113.3; 75.8; 25.8; 18.3; -4.6; -4.8. ESI-MS: 271 (70, $[M + Na]^+$).

Methyl (3R,5E,7S)-3,7-*Bis*{[(tert-*butyl*)(*dimethyl*)*silyl*]*oxy*}-7-*phenylhept-5-enoate* (**4**). To a soln. of **5** (0.24 g, 0.93 mmol) and **6** (0.34 g, 1.37 mmol) in CH₂Cl₂ (5 ml), 10 mol-% *Grubbs*' catalyst II (**A**; 0.078 g, 0.09 mmol) was added and stirred at r.t. for 24 h under N₂. Most of the solvent was then distilled off, and the concentrated soln. was left to be stirred at r.t. for 2 h under air bubbling in order to decompose the catalyst. The mixture was evaporated to dryness to give a brown residue, which was purified by CC (SiO₂; 1% AcOEt/hexane) to give **4** (0.26, 60%) as a yellow color liquid, and *dimethyl* (3R,5E₂8R)-3,8-*bis*{(tert-*butyl*)(*dimethyl*)*silyl*]*oxy*]*dec-5-enedioate* (**12**) (0.022, 5%) as colorless syrup.

Data of **4**: $[\alpha]_{25}^{25} = -40.8 \ (c = 0.75, CHCl_3)$. IR (neat): 3452, 2931, 2857, 1742, 1634, 1253, 1087, 835, 775. ¹H-NMR (300 MHz, CDCl_3): 7.31 – 7.16 (*m*, 5 H); 5.72 – 5.55 (*m*, 1 H); 5.54 – 5.35 (*m*, 1 H); 5.11 (*d*, J = 5.2, 1 H); 4.24 – 4.12 (*m*, 1 H); 3.64 (*s*, 3 H); 2.47 – 2.34 (*m*, 2 H); 2.28 – 2.17 (*m*, 2 H); 0.93 (*s*, 9 H); 0.86 (*s*, 9 H); 0.087 (*s*, 3 H); 0.08 (*s*, 3 H); 0.06 (*s*, 3 H); 0.05 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl_3): 172.1; 137.0; 128.1; 126.8; 125.8; 124.7; 117.7; 75.3; 69.0; 51.4; 41.8; 40.2; 25.6; 25.8; 17.9; 17.5; -4.2; -4.5; -4.7; -5.0. ESI-MS: 501 (100, $[M + Na]^+$). HR-MS: 501.2821 ($C_{26}H_{46}NaO_4Si^{\pm}_{\pm}$; calc. 501.2832).

Data of **12**: $[\alpha]_{25}^{25} = -53.1$ (c = 0.5, CHCl₃). IR (neat): 3078, 2932, 2858, 1711, 1644, 1433, 1254, 1090, 834, 776. ¹H-NMR (300 MHz, CDCl₃): 5.72–5.57 (m, 2 H); 4.31 (quint, J = 5.8, 2 H); 3.82 (s, 6 H); 2.58–2.53 (m, 4 H); 2.39 (t, J = 5.2, 4 H); 1.04 (s, 18 H); 0.23 (s, 6 H); 0.20 (s, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 172.3; 129.2; 69.8; 51.8; 42.4; 40.9; 25.8; 18.2; -4.0; -5.1. ESI-MS: 489 (28, $[M + H]^+$), 511 (100, $[M + Na]^+$). HR-MS: 511.2892 ($C_{24}H_{48}NaO_6Si_2^+$; calc. 511.2887).

Conversion of **12** to **4**. To a soln. of **12** (0.010 g, 0.02 mmol) and **6** (0.007 g, 0.02 mmol) in CH₂Cl₂ (1 ml), 10 mol-% **A** (0.004 g, 0.047 mmol) was added, and the mixture was stirred at r.t. for 24 h under N₂. Most of the solvent was then distilled off, and the concentrated soln. was left to be stirred at r.t. for 2 h under air bubbling in order to decompose the catalyst. The mixture was evaporated to dryness to give a brown residue, which was purified by CC (SiO₂; 1% AcOEt/hexane) to give **4** (0.005, 60%).

Methyl (3R,5R,6S,7R)-3,7-*Bis*[[(tert-*butyl*)(*dimethyl*)*sily*]*joxy*]-5,6-*dihydroxy*-7-*phenylheptanoate* (3). To a stirred soln. of **4** (0.24 g, 0.50 mmol) in acetone/H₂O 4 :1 (2 ml), NMO (0.11 ml, 1 mmol) and 2 ml of 1M toluene soln. of OsO₄ were added at r.t., and the mixture was stirred for 24 h. The reaction was quenched with Na₂SO₃ (0.2 g), the mixture was filtered and washed with AcOEt, and the resulting filtrate was washed with H₂O (4 ml), followed by brine (4 ml). The combined org. layers were dried (Na₂SO₄), evaporated *in vacuo*, and purified by CC (SiO₂; 5% AcOEt/hexane) to afford **3** (0.19 g, 75%). Syrupy liquid. [α]²⁵₇ = -34.1 (c = 0.2, CHCl₃). IR (neat): 3451, 2856, 1739, 1639, 1254, 836, 777, 700. ¹H-NMR (500 MHz, CDCl₃): 757 - 7.38 (m, 5 H); 5.10 (d, J = 4.5, 1 H); 4.54 - 4.39 (m, 1 H); 4.22 (d, J = 10.5, 1 H); 3.83 (s, 3 H); 3.54 - 3.43 (m, 1 H); 3.38 (br. s, OH); 2.70 - 2.54 (m, 3 H); 2.09 - 1.87 (m, 1 H); 1.12 (s, 9 H); 0.97 (s, 9 H); 0.30 (s, 3 H); 0.21 (s, 3 H); 0.02 (s, 3 H); 0.09 (s, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 171.3; 141.0; 128.4; 127.6; 126.2; 78.7; 66.6; 65.5; 64.7; 51.4; 42.7; 41.1; 25.9; 25.8; 18.2; 17.9; -4.4; -4.6; -4.77; -5.02. ESI-MS: 513 (42, [M + H]⁺), 535 (100, [M + Na]⁺). HR-MS: 535.2891 (C₂₆H₄₈NaO₆Si[±]; calc. 535.2887).

(4R,6R)-6-[(1R,2R)-1,2-Dihydroxy-2-phenylethyl]-4-hydroxytetrahydro-2H-pyran-2-one (1). To a stirred soln. of **3** (0.16 g, 0.31 mmol) in MeCN (2 ml), *Amberlyst 15* (0.005 g) was added at r.t. and stirred for 2 h. The mixture was filtered and washed with AcOEt, and the resulting filtrate was evaporated *in vacuo* and purified by CC (SiO₂; 35% AcOEt/hexane) to afford **1** (0.073 g, 93%). Colorless needles. $[\alpha]_{D}^{25} = -63.1$ (c = 0.3, CHCl₃). IR (neat): 3423, 2920, 2850, 1720, 1656, 1460, 1219, 606. ¹H-NMR

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 $(500 \text{ MHz}, \text{CDCl}_3): 7.47 - 7.25 (m, 5 \text{ H}); 4.91 (d, J = 7.8, 1 \text{ H}); 4.73 (dd, J = 4.4, 9.8, 1 \text{ H}); 4.28 (quint., J = 6.8, 1 \text{ H}); 3.7 (d, J = 8.8, 1 \text{ H}); 2.86 (dd, J = 5.4, 17.2, 1 \text{ H}); 2.55 (dd, J = 7.3, 17.2, 1 \text{ H}); 2.20 - 2.14 (m, 1 \text{ H}); 2.08 - 1.99 (m, 1 \text{ H}). ^{13}\text{C-NMR} (75 \text{ MHz}, \text{CDCl}_3): 172.1; 141.3; 128.5; 127.8; 127.2; 78.0; 68.9; 67.0; 66.8; 41.1; 40.1. ESI-MS: 275 (100, [M + Na]^+). HR-MS: 275.0907 (C_{13}\text{H}_{16}\text{NaO}_{5}^+; \text{ calc. } 275.0895).$

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