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Regioselective Synthesis of β- and γ-Thujaplicins

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Abstract—β-Thujaplicin (hinokitiol) **1** and γ-thujaplicin **2**, as the first naturally occurring monocyclic tropolone, were regioselectively synthesized from (*R*)-(+)-limonene, by using different dienyl silyl ether intermediates, **7** and **10**, in 18% overall yield via 11 steps and 22% overall yield via 10 steps, respectively.

Introduction

β- and γ-Thujaplicins (4- and 5-isopropyltropolones) were isolated from *Chamaecyparis taiwanesis* Masamune et Suzuki[1] and *Thuja plicata* D. Don[2] as naturally occurring monocyclic tropolones, and these are the first examples of non-benzenoid aromatics. Particularly, their antibacterial and antifungal activities, which evidently impart decay-resistant property to the heart-wood, have aroused much interest.[3]

Various synthetic approaches to these compounds have traditionally been achieved by the cycloaddition of isopropylcyclopentadiene and dichloro ketene,[4] 1,3-dipolar cycloaddition of 5-isopropyl-1-methyl-3-oxidopyridinium,[5] the ring expansion of 2-isopropylcyclohexanone,[6] and regiocontrolled hydroxylation of oxyallyl [4+3] cycloadducts.[7f] Despite the considerable theoretical, biological and synthetic interest in tropolones, study on regioselective synthetic routes from the same intermediate to these compounds has not been carried out so far.[7] (Fig. 1).

In this paper, we describe a novel and useful regioselective synthesis of β-thujaplicin (hinokitiol) **1** and γ-thujaplicin **2** starting from commercially available (*R*)-(+)-limonene by construction of the cycloheptanone ring based on the Lewis acid-promoted intramolecular aldol condensation of acetal with enol silyl ether,[8] and regioselective α-hydroxylation of the enone via dienyl silyl ethers prepared either kinetically or thermodynamically.

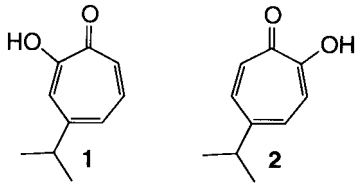

Figure 1.

The synthesis of **1** and **2** can be planned according to the retrosynthetic analysis shown in Scheme 1. It is conceivable that **1** and **2** will be constructed from the key intermediates, the dienyl silyl ethers **A** and **B**, by the regioselective α-hydroxylation and oxidation. Both **A** and **B** are derivable from the common cycloheptanone **C**, which should be obtained by using the Lewis acid-mediated intramolecular aldol reaction via enol silyl ether **D**, derivable from (*R*)-(+)-limonene.

Results and Discussion

Scheme 2 shows our synthetic route leading to **1** and **2**.

The kinetic dienyl silyl ether **4** was obtained from the known acetal ketone **3**[9] in high yield by employing lithium diisopropylamide (LDA, 1.0 equiv.) and chlorotrimethylsilane (TMSCl, 2.0 equiv., THF, −78°C).[10] Cyclization to the seven-membered ring was investigated with a variety of Lewis acids (TMSOTf, $ZnBr_2 \cdot Et_2O$ and $TiCl_4$). In this reaction with TMSOTf or $ZnBr_2 \cdot Et_2O$, the yield of the desired cycloheptanone **5** was quite low (below 30%), and considerable amounts of the aldehyde were detected in the NMR spectra of the crude products. When the reaction was carried out with a catalytic amount of $TiCl_4$, the acetal group of **4** was hydrolyzed into the aldehyde. On the contrary, the reaction with $TiCl_4$ (1.2 equiv., CH_2Cl_2, −78°C) was found to proceed quite nicely, giving an inseparable diastereomeric mixture (1:1) of **5** in 82% yield via two steps.

Keywords: β-thujaplicin (hinokitiol); γ-thujaplicin; thermodynamic dienyl silyl ether; limonene.

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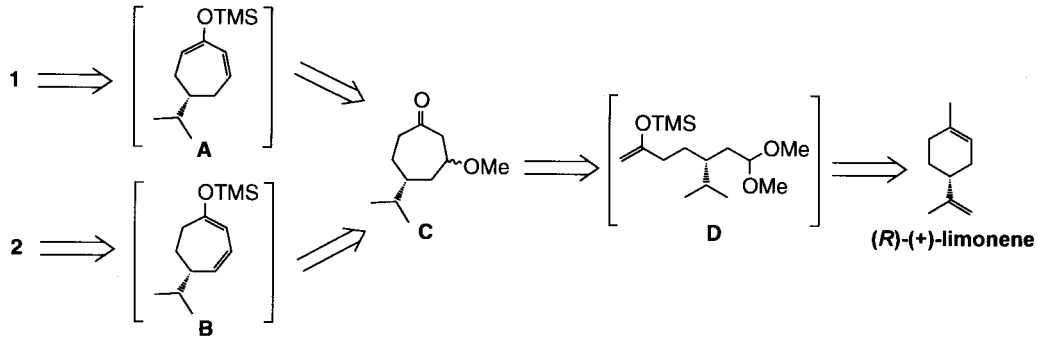
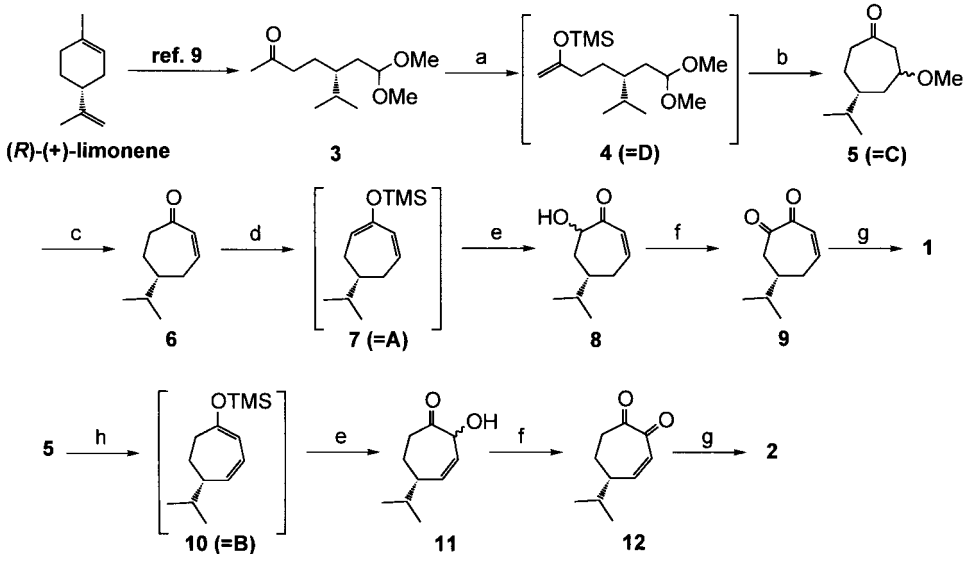


Scheme 1.



Scheme 2.

Elimination of the methoxyl group of **5** was achieved by refluxing with a catalytic amount (10% (W/W)) of *p*-toluenesulfonic acid and molecular sieves (4 Å) in dry benzene to give cycloheptenone **6** in 63% yield. A dienyl silyl ether **7**, quite unstable, was obtained by the reaction with LDA (1.0 equiv.) and TMSCl (2.0 equiv., THF, −15°C) in 90% yield after non-aqueous workup. Without further purification, oxidation of **7** was carried with MCPBA (1.2 equiv., *n*-hexane, 0°C); then, treatment with triethylamine trihydrofluoride ($Et_3N{\cdot}3HF$, 1.0 equiv., CH_2Cl_2)[11] gave an inseparable diastereomeric mixture (1:1) of **8** in 80% yield via two steps.

This α-hydroxy cycloheptenone **8** was a very unstable compound, which was easily oxidized. Oxidation of alcohol **8** with Dess–Martin periodinane[12] in CH_2Cl_2 cleanly afforded cycloheptenedione **9** in 88% yield, which was also unstable and easily enolizable.

The final step was the aromatization of **9** to β-thujaplicin **1**. When 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[13] was employed as the dehydrogenating reagent, the desired **1** could not be obtained. So, we examined bromination of **9** with pyrrolidone hydrotribromide (PHT)[14] and successive dehydrobromination with $LiBr–Li_2CO_3$ in DMF, and succeeded in obtaining **1** in 71% yield via the two steps. Comparison of the ^1H NMR data of the synthetic β-thujaplicin **1** with those of the literature[1] completely confirmed the identity of **1**.

For the synthesis of γ-thujaplicin **2**, the thermodynamically more stable dienyl silyl ether **10** was required, but the desired product could not be obtained by using several bases (NaH, KH, and Et_3N) from **6**. However, one-pot reaction of **5** with iodotrimethylsilane (TMSI, 1.3 equiv.) and hexamethyldisilazane (HMDS, 1.5 equiv., CH_2Cl_2, −15°C) was found to proceed very nicely, and the desired product **10** was obtained in 92% yield. The regiochemical outcome of the reaction was established by observation of the coupling patterns among the $C_2–C_5$ protons in the H–H COSY spectrum (300 MHz, $CDCl_3$). This allowed a characteristic assignment of the C_4–H and C_5–H coupling and the chemical shift (δ=5.49, dd, J=4, 12 Hz) of the C_4-H, which showed that **10** had been prepared from **5**. This process may be applicable to the preparation of thermodynamically stable dienyl silyl ethers from linear and/or cyclic β-alkoxy ketones.

Similarly to the synthesis of **1**, we carried out MCPBA oxidation and treatment of $Et_3N{\cdot}3HF$ and obtained an inseparable diastereomeric mixture (1:1) of α-hydroxy cycloheptenone 11 in 55% yield via two steps. Dess–Martin

oxidation (94%) of alcohol **11**, bromination with PHT and dehydrobromination with $LiBr–Li_2CO_3$ afforded **2** from **12** in 75% yield via two steps. The ^1H NMR data of synthetic **2** were completely indistinguishable from those reported.[1]

In summary, both β-thujaplicin **1** and γ-thujaplicin **2** were synthesized from (*R*)-(+)-limonene in overall 18% yield via 11 steps and 22% yield via 10 steps, respectively. The key step was the regioselective formation of the different types of dienyl silyl ethers **7** and **10** from the same intermediate **5** and their conversion to isomeric ketols **8** and **11**, respectively.

Experimental

Infrared spectra (IR) were measured on a Jasco FT/IR-230 spectrometer. Proton magnetic resonance spectra (^1H NMR) were recorded at 300 MHz on JEOL JNM-AL 300 spectrometer. Chemical shifts are reported in parts per million (δ) relative to internal chloroform (δ 7.24). Optical rotations were measured on a Jasco DIP-1000 polarimeter. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm Merck silica gel 60 F_{254} precoated glass-backed plates. Compounds were visualized by ultraviolet light (254 nm), iodine vapor, iron(III) chloride in chloroform solution, or phosphomolybdic acid spray reagents. Column chromatography was performed on Merck silica gel 60 and Cica silica gel 60 N (neutral). All solvents used were of reagent grade. Tetrahydrofuran was distilled over benzophenone and sodium prior to use. Dichloromethane and benzene were distilled from calcium hydride and stored over 4 Å molecular sieves.

(3*R*)-3-Isopropyl-1,1-dimethoxyheptan-6-one, 3. This compound was prepared from (*R*)-(+)-limonene according to the known procedure[9] in 87% yield via two steps. Analytical data (bp, $[\alpha]_D$, IR, and ^1H NMR) of **3** were completely indistinguishable from those reported.[9]

(5*R*)-5-Isopropyl-3-methoxycycloheptanone, 5. To a solution of diisopropylamine (4.2 ml, 30.1 mmol) in dry THF (50 ml) was added *n*-butyllithium (18.5 ml, 27.8 mmol, 1.5 M in *n*-hexane) at −15°C and the mixture was allowed to warm up to 0°C for 30 min and then cooled to −78°C. A solution of **3** (5.0 g, 23.2 mmol) in dry THF (20 ml) was added over 10 min and the mixture was stirred at −78°C for 1 h under an atmosphere of N_2. Chlorotrimethylsilane (TMSCl, 8.8 ml, 69.5 mmol) was added, and the mixture was stirred for 2 h while the temperature was warmed slowly up to room temperature.

The solvent was removed under reduced pressure and dry *n*-pentane was added to the residue. The pentane extract was filtered through a celite pad and the filtrate was evaporated to afford 6.0 g of crude enol silyl ether **4** (=**D**) as a pale yellow oil, which was directly used for the next step without further purification.

4. IR ν_{max} (film) 2960, 1640, 1254, 1122, 1060, 1019, 853 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=4.41 (t, *J*=6 Hz, 1H), 4.01 (d, *J*=6 Hz, 2H), 3.29 (s, 3H), 3.28 (s, 3H), 1.98 (t, *J*=8 Hz, 2H), 1.75–1.33 (m, 6H), 0.82 (d, *J*=7 Hz, 3H), 0.81 (d, *J*=7 Hz, 3H), 0.18 (s, 9H).

To a solution of crude **4** (6.0 g) in dry CH_2Cl_2 (80 ml) was rapidly added $TiCl_4$ (24.0 ml, 24.1 mmol, 1.0 M in CH_2Cl_2) at −78°C and the whole was stirred for 10 min under an atmosphere of N_2. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ solution and extracted with $CH_2Cl_2–H_2O$. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified with SiO_2 column chromatography (EtOAc–*n*-hexane=1:8) to give 3.1 g (71% in two steps) of β-methoxycycloheptanone **5** (=**C**) as a pale yellow oil.

5. IR ν_{max} (film) 2955, 1702, 1714, 1463, 1369, 1250, 1194, 1091, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=3.68 (bt, *J*=6 Hz, 1H), 3.32 (bs, 3H), 3.29 (bs, 3H), 2.91–2.05 (m, 4H), 1.70–1.25 (m, 6H), 0.91–0.81 (m, 6H); Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%. Found: C, 71.85; H, 10.82%.

(5*R*)-5-Isopropyl-2-cyclohepten-1-one, 6. To a solution of **5** (2.5 g, 10.1 mmol) in dry C_6H_6 (50 ml) was added *p*-toluenesulfonic acid (0.5 g, 2.7 mmol) and molecular sieves (4 Å) (10.0 g), and then the mixture was refluxed for 1 h under an atmosphere of N_2. The reaction mixture was diluted with EtOAc and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$ solution, water, and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residual oil was purified by SiO_2 column chromatography (EtOAc–*n*-hexane=1:6) to give 1.1 g (63%) of **6** as a pale yellow oil.

6. $[\alpha]_D^{23}$=+41.9 (*c*=1.0, $CHCl_3$); IR ν_{max} (film) 2960, 2880, 1665, 1460, 1395, 1260, 1090, 922, 805 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=6.60 (dd, *J*=2, 12 Hz, 1H), 5.97 (dd, *J*=1, 12 Hz, 1H), 2.69–2.49 (m, 2H), 2.48–2.21 (m, 2H), 1.82–1.49 (m, 3H), 0.88 (d, *J*=7 Hz, 3H), 0.87 (d, *J*=7 Hz, 3H); Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%. Found: C, 78.70; H, 10.54%.

(5*S*)-7-Hydroxy-5-isopropyl-2-cyclohepten-1-one, 8. To a solution of diisopropylamine (1.2 ml, 8.2 mmol) in dry THF (20 ml) was added *n*-butyllithium (10.5 ml, 15.8 mmol, 1.5 M in *n*-hexane) at −15°C, and the mixture was allowed to warm up to 0°C for 30 min and then recooled to −15°C. A solution of **6** (1.0 g, 6.6 mmol) in THF (10 ml) was added over 10 min and the mixture was stirred at −15°C for 30 min under an atmosphere of N_2. TMSCl (1.7 g, 13.1 mmol) was added and the reaction mixture was stirred for 30 min while the temperature was warmed slowly to room temperature.

The solvent was removed under reduced pressure and dry *n*-pentane was added to the residue. The pentane extract was filtered through a celite pad and then evaporated to afford 1.4 g (90%) of crude dienyl silyl ether **7** (=**A**) as a pale yellow oil, which was directly used for the next step without further purification.

To a solution of **7** (1.3 g, 6.0 mmol) in dry *n*-hexane (30 ml) was added *m*-chloroperbenzoic acid (MCPBA, 1.3 g,

7.2 mmol) at −15°C and the mixture was stirred at room temperature for 4 h. The reaction mixture was filtered through a Celite pad and the solvent was removed under reduced pressure. The residue was mixed with dry CH_2Cl_2 (50 ml) and triethylamine trihydrofluoride ($Et_3N{\cdot}3HF$, 1.0 g, 6.0 mmol) and the solution was stirred for 2 h at room temperature. The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. The solution was removed and the residue was purified by neutral SiO_2 column chromatography (EtOAc–*n*-hexane=1:8) to give 0.8 g (80% in two steps) of a diastereomeric mixture (1:1) of **8** as a clear oil.

8. IR ν_{max} (film) 3457, 2958, 2873, 1667, 1463, 1391, 1261, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=6.94 (dd, *J*=6, 12 Hz, 0.5H), 6.68 (dd, *J*=6, 12 Hz, 0.5H), 6.14 (dt, *J*=<1, 12 Hz, 1H), 4.32 (ddd, *J*=2, 3, 12 Hz, 0.5H), 4.14 (ddd, *J*=2, 3, 12 Hz, 0.5H), 4.02 (d, *J*=2 Hz, 0.5H), 3.81 (d, *J*=2 Hz, 0.5H), 2.48–2.27 (m, 1H), 2.25–2.10 (m, 1H), 2.05–1.85 (m, 1H), 1.72–1.40 (m, 2H), 0.90 (d, *J*=7 Hz, 3H), 0.87 (d, *J*=7 Hz, 3H); HRMS (FAB, glycerol, 1 N HCl added) (M^++1−H_2O) Calcd for $C_{10}H_{15}O$: 151.1044; Found: 151.1116.

(5*S*)-5-Isopropyl-1-trimethylsilyloxymethyl-1,3-cycloheptene, 10. To a solution of **5** (1.5 g, 8.2 mmol) in dry CH_2Cl_2 (30 ml) was added iodotrimethylsilane (TMSI, 1.4 ml, 9.8 mmol) and hexa-methyldisilazane (HMDS, 2.2 ml, 1.1 mmol) at −78°C under an atmosphere of N_2. The reaction mixture was stirred for 4 h while the temperature was warmed slowly to room temperature.

The solvent was removed under reduced pressure and dry *n*-pentane was added to the residue. The pentane extract was filtered through a florisil column and then evaporated to afford 1.8 g (90%) of dienyl silyl ether **10** (=**B**) as a pale yellow oil, which was used for the next step without further purification.

10. IR ν_{max} (film) 2994, 1507, 1347, 1109, 999, 794 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=5.56 (ddd, *J*=2, 7, 12 Hz, 1H), 5.49 (dd, *J*=4, 12 Hz, 1H), 5.13 (d, *J*=7 Hz, 1H), 2.45–2.30 (m, 2H), 2.15–2.05 (m, 1H), 1.75–1.61 (m, 3H), 0.90 (d, *J*=7 Hz, 3H), 0.89 (d, *J*=7 Hz, 3H), 0.18 (s, 9H).

(5*S*)-2-Hydroxy-5-isopropyl-3-cyclohepten-1-one, 11. In the same manner as described above, silyl enol ether **10** (1.0 g, 4.5 mmol) gave 0.4 g (55% in two steps) of a diastereomeric mixture of **11** as a clear oil.

11. IR ν_{max} (film) 3457, 2958, 1667, 1463, 1391, 1261, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=5.76 (ddd, *J*=3, 5, 12 Hz, 0.5H), 5.52 (ddd, *J*=3, 5, 12 Hz, 0.5H), 5.44 (ddd, *J*=2, 5, 12 Hz, 0.5H), 5.36 (ddd, *J*=2, 5, 12 Hz, 0.5H), 5.30 (dd, *J*=3, 5 Hz, 0.5H), 5.14 (dd, *J*=3, 5 Hz, 0.5H), 2.86–2.71 (m, 1H), 2.64–2.46 (m, 1H), 2.26–2.10 (m, 1H), 2.06–1.74 (m, 3H), 0.93 (d, *J*=7 Hz, 3H), 0.92 (d, *J*=7 Hz, 3H); HRMS (FAB, glycerol, 1 N HCl added) (M^++1−H_2O) Calcd for $C_{10}H_{15}O$: 151.1044; Found: 151.1078.

(6*S*)-6-Isopropyl-3-cycloheptene-1,2-dione, 9. To a solution of **8** (0.5 g, 3.0 mmol) in dry CH_2Cl_2 (20 ml) was added Dess–Martin periodinane (1.5 g, 3.6 mmol) and the mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with Et_2O, washed with saturated aqueous $NaHCO_3$ solution and brine and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by neutral SiO_2 column chromatography (EtOAc–*n*-hexane=1:10) to give 0.4 g (88%) of cycloheptenedione **9** as a pale yellow oil.

9. IR ν_{max} (film) 2962, 2875, 1714, 1668, 1469, 1392, 1285, 934 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=6.85 (ddd, *J*=4, 6, 12 Hz, 1H), 6.20 (ddd, *J*=1, 2, 12 Hz, 1H), 2.80–2.61 (m, 1H), 2.59–2.50 (m, 1H), 2.45–2.30 (m, 2H), 2.10–1.91 (m, 1H), 1.85–1.67 (m, 1H), 0.93 (d, *J*=7 Hz, 3H), 0.93 (d, *J*=7 Hz, 3H); Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. Found: C, 71.91; H, 8.53%.

(5*S*)-5-Isopropyl-3-cycloheptene-1,2-dione, 12. In the same manner as described above, **11** (200 mg, 1.203 mmol) gave 186 mg (94%) of **12** as a pale yellow oil.

12. IR ν_{max} (film) 2960, 1714, 1668, 1463, 1390, 1283, 1104, 935, 825 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=6.73 (ddd, *J*=1, 4, 13 Hz, 1H), 6.23 (dd, *J*=3, 13 Hz, 1H), 2.85 (ddd, *J*=3, 7, 17 Hz, 1H), 2.60 (ddd, *J*=3, 11, 17 Hz, 1H), 2.40–2.30 (m, 1H), 2.02 (dtdd, *J*=1, 3, 7, 14 Hz, 1H), 1.92 (dh, *J*=2, 7 Hz, 1H), 1.75 (dddd, *J*=4, 7, 11, 14 Hz, 1H), 0.96 (d, *J*=7 Hz, 3H), 0.95 (d, *J*=7 Hz, 3H); Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. Found: C, 72.12; H, 8.63%.

β-Thujaplicin (hinokitiol), 1

To a solution of **9** (150 mg, 0.902 mmol) in dry THF (10 ml) was added pyrrolidone hydrotribromide (PHT, 490 mg, 0.988 mmol) and the mixture was stirred at room temperature for 1 h under an atmosphere of N_2. The reaction mixture was diluted with Et_2O and filtered through a celite pad. The filtrate was washed with saturated aqueous $NaHCO_3$ solution and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was dissolved in dry DMF (15 ml) and the mixture was refluxed with LiBr (100 mg, 1.152 mmol) and Li_2CO_3 (85 mg, 1.152 mmol) for 2 h under an atmosphere of N_2. The cooled reaction mixture was treated with 1N HCl solution and extracted with Et_2O. The extract was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by SiO_2 column chromatography (EtOAc–*n*-hexane=1:1) to give 100 mg (71% in two steps) of **1** as a white solid.

1. Mp 49–50°C (lit. 52–52.5°C);[1] IR ν_{max} (film) 3196, 2965, 2872, 1612, 1543, 1471, 1365, 947, 824 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=7.33–7.18 (m, 3H), 6.94 (d, *J*=10 Hz, 1H), 2.87 (h, *J*=7 Hz, 1H), 1.25 (d, *J*=7 Hz, 6H); Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. Found: C, 73.28; H, 7.37%.

γ-Thujaplicin, 2

In the same manner as described above, **12** (70 mg, 0.421 mmol) gave 50 mg (75% in two steps) of **2** as an oil.

2. Mp 78–79°C (lit. 80–81°C);[2] IR ν_{max} (film) 3206, 2965, 1617, 1556, 1468, 1265, 857 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ=7.27 (d, J=2 Hz, 4H), 2.84 (h, J=7 Hz, 1H), 1.21 (d, J=7 Hz, 6H); Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. Found: C, 73.18; H, 7.64%.

References

1. Nozoe, T. *Nature (London)* **1951**, *167*, 1055.
2. Erdtman, H.; Gripenberg, J. *Nature (London)* **1948**, *161*, 716.
3. Baillie; Freeman; Cook; Somerville *Nature (London)* **1950**, *166*, 65.
4. Tanaka, K.; Yoshikoshi, A. *Tetrahedron* **1971**, *27*, 4889.
5. Tamura, Y.; Saito, T.; Kiyokawa, H.; Chen, L. C.; Ishibashi, H. *Tetrahedron Lett.* **1977**, *18*, 4075.
6. Miyashita, M.; Hara, S.; Yoshikoshi, A. *J. Org. Chem.* **1987**, *52*, 2602.
7. For previous syntheses of 1, see: (a) Nozoe, T.; Asao, T. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1452. (b) Takaya, H.; Hayakawa, Y.; Makino, S.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1778. (c) Franck-Neumann, M.; Brion, F.; Martina, D. *Tetrahedron Lett.* **1978**, *19*, 5033. (d) Banwell, M. G. *Aust. J. Chem.* **1991**, *44*, 1. (e) Banwell, M. G.; Cameron, J. M.; Collis, M. P.; Crisp, G. T.; Gable, R. W.; Hamel, E.; Lambert, J. N.; Mackay, M. F.; Reum, M. E.; Scoble, J. A. *Aust. J. Chem.* **1991**, *44*, 705. (f) Lee, J. C.; Cho, S. Y.; Cha, J. K. *Tetrahedron Lett.* **1999**, *40*, 7675, and references cited therein.
8. Mukaiyama, T. *Tetrahedron* **1999**, *55*, 8609.
9. Kitahara, T.; Mori, M.; Mori, K. *Tetrahedron* **1987**, *43*, 2689.
10. Krafft, M. E.; Holton, R. A. *Tetrahedron Lett.* **1983**, *24*, 1345.
11. Rubottom, G. M.; Gruber, J. M.; Juve, H. D.; Charleson, D. A. *Org. Synth.* **1986**, *64*, 118.
12. Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.
13. Raddo, P. D.; Harvey, R. G. *Tetrahedron Lett.* **1988**, *29*, 3885.
14. Hankovszky, H. O.; Hideg, K.; Sar, P. C.; Lovas, M. J.; Jerkovich, G. S. *Synthesis* **1990**, 59.