HETEROCYCLES, Vol. 68, No. 12, 2006, pp. 2579 - 2585. © The Japan Institute of Heterocyclic Chemistry
Received, 12th September, 2006, Accepted, 23rd October, 2006, Published online, 27th October, 2006. COM-06-10885

FIRST SYNTHESIS OF *TRANS*- AND *CIS*-DENDROCHRYSANINES

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Abstract – *Trans*- and *cis*-dendrochrysanines (**1** and **2**), isolated from the stems of *Dendrobium chrysanthum* Wall., were first synthesized from L-proline. The absolute configuration of **1** and **2** was established to be *S* by the syntheses.

INTRODUCTION

Trans- and *cis*-dendrochrysanines (**1** and **2**)[1] were isolated from the stems of *Dendrobium chrysanthum* Wall.[2] by Z. Wang and co-workers in 2005 and used in traditional Chinese medicine. These structures were identified as the *N-trans*-cinnamoyl-2-oxopropyrrolidine (**1**) and the *N-cis*-cinnamoyl-2-oxopropyrrolidine (**2**), based on extensive 2D-NMR (^{1}H-^{1}H COSY, HMQC, and HMBC) experiments. The absolute configuration of **1** and **2**, however, has been estimated by comparing their optical rotations and CD curve with those of known related compounds, *N-cis*-cinnamoly-L-proline and *N-cis*-cinnamoyl-L-2-methyl pyrrolidine.[3] In the course of studying cysteine protease inhibitors,[4,5] we have interested in these natural products, since their α,β-unsaturated carbonyl structure is known to be a typical functional group for the thiol group of cysteine proteases. Here, we describe the first synthesis of *trans*- and *cis*-dendrochrysanines (**1** and **2**) as well as the determination of their absolute configurations, prior to medicinal studies of those natural products.

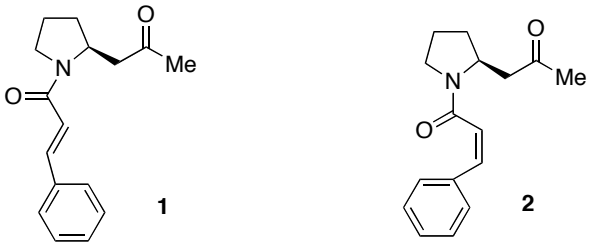
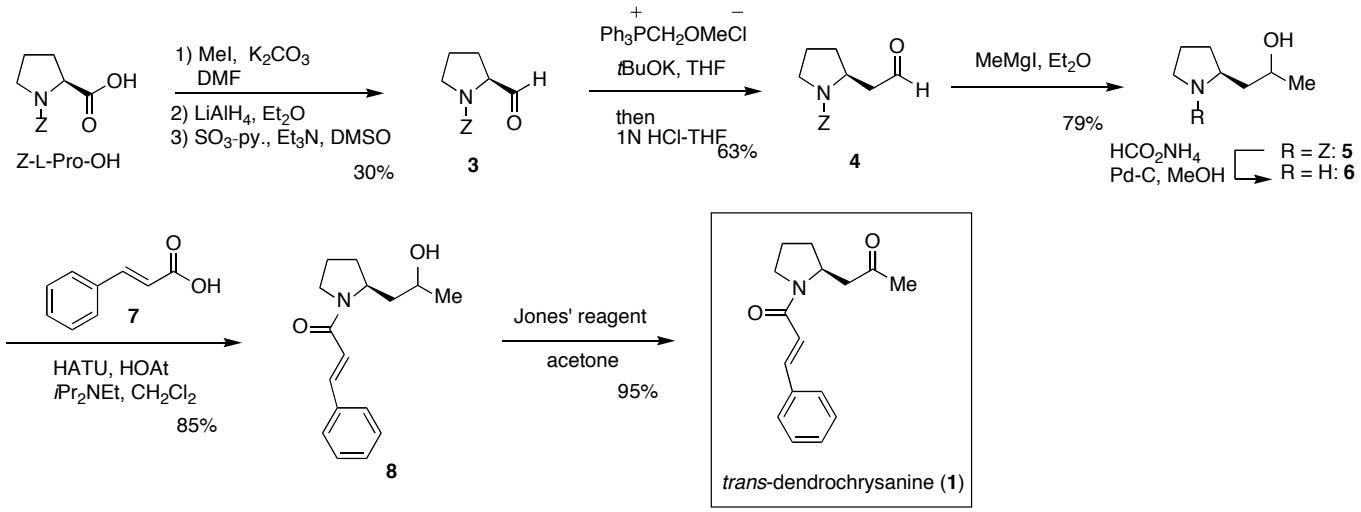


Figure Structure of *trans*-dendrochrysanine (**1**) and *cis*-dendrochrysanine (**2**)

RESULTS AND DISCUSSION

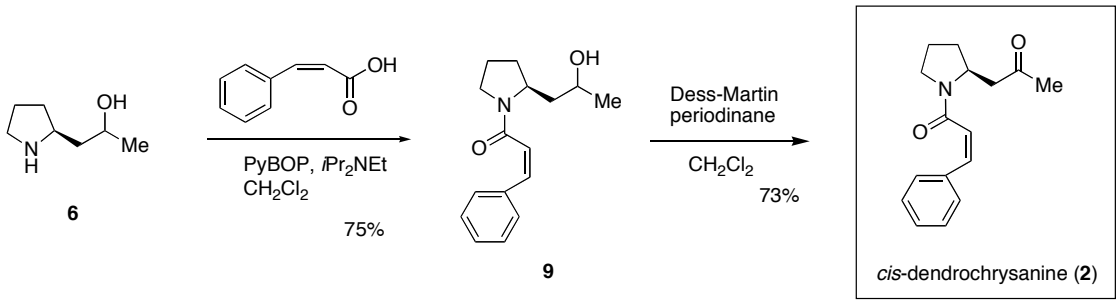
Trans-dendrochrysanine (**1**) was synthesized according to the route shown in Scheme 1. Z-L-Proline (Z-L-Pro-OH) was first transformed into Z-prolinal (**3**) through protection of the carboxyl group with iodomethane, and aldehyde transformation via the alcohol in a overall yield of 30%.[6] The optical purities of **3** and the intermediate alcohol were determined to be >98%ee by HPLC using chiral column. A subsequence Wittig reaction with (methoxymethyl)triphenylphosphonium chloride and potassium *tert*-butoxide in THF gave a one-carbon extended methoxy olefin product, which was then treated with 1N HCl in THF to give the desired aldehyde (**4**) in 63% yield. Enantiomeric excess of aldehyde (**4**) was determined to be 98%ee by HPLC using chiral column. A Grignard reaction of aldehyde (**4**) with methylmagnesium iodide in ether afforded two diastereomeric alcohols (**5**) as a 1:1.5 mixture in 79% yield. Deprotection of the Z group in the presence of 5% palladium on carbon in a hydrogen atmosphere gave the pyrrolidine (**6**), which was coupled with *trans*-cinnamic acid (**7**) by a reaction with O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU)[9]/ 1-hydroxy-7-azabenzotriazole (HOAt)[10]/ *N*, *N*-diisopropylethylamine in CH_2Cl_2 to afford **8** as a diastereoisomeric mixture in 85% yield. Finally, the alcohol (**8**) was oxidized with Jones' reagent to give *trans*-dendrochrysanine (**1**), $[\alpha]_D^{20}$ -11.8° (*c* 0.15, $CHCl_3$) [lit.; $[\alpha]_D^{20}$ -19.2° (*c* 3.4, $CHCl_3$)] in 95% yield. The ^{1}H- and ^{13}C-NMR spectra of the synthetic **1** were in good agreement with those of natural **1**.



Scheme 1. Synthesis of *trans*-dendrochrysanine (**1**)

Similarly, *cis*-dendrochrysanine (**2**) was synthesized from pyrrolidine (**6**) in 2 steps (Scheme 2). The pyrrolidine (**6**) was coupled with *cis*-cinnamic acid[11] using HATU/ HOAt/ *N*, *N*-diisopropylethylamine in CH_2Cl_2 as above. The condensation product, however, was obtained with only 5% yield probably deu to the formation of stable adduct from the *cis*-cinnamic acid and HOAt. Desired alcohol (**9**) was obtained in 75% yield when benzotriazol-1-yl-oxy-tris–pyrrolidino-phosphonium hexafluorophosphate (PyBOP)[12] was employed instead of HOAt. Finally, oxidation of **11** with Dess-Martin periodinane[13] in CH_2Cl_2

afforded *cis*-dendrochrysanine (**2**), $[\alpha]_D^{24}$ -14.5° (*c* 0.04, $CHCl_3$) [lit.; $[\alpha]_D^{20}$ -17.7° (*c* 3.5, $CHCl_3$)]. The ^{1}H- and ^{13}C-NMR spectra of the synthetic **2** were in good agreement with those of natural **2**.



Scheme 2. Synthesis of *cis*-dendrochrysanine (**2**)

In conclusion, we have completed the first synthesis of *trans*- and *cis*-dendrochrysanines (**1** and **2**). The absolute structure of these compounds has been established to be (2*S*)-*N*-*trans*-cinnamoly-2-oxopropyrrolidine for **1** and (2*R*)-*N*-*cis*-cinnamoly-2-oxopropyrrolidine for **2**.

EXPERIMENTAL

General Experimental Procedures. All manipulations were conducted under an inert atmosphere (N_2). All solvents were of reagent grade. THF was distilled from sodium and benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. All commercial reagents were of the highest purity available. Analytical TLC was performed on silica gel (60 F-254, Plates 0.25 mm). Column chromatography was carried out on Wakogel 60 (particle size, 0.063-0.200 mm). ^{1}H-, and ^{13}C-NMR were recorded on a JEOL JNM-EX-400 or Bruker AVANCEII-300. Chemical shifts are expressed in ppm relative to TMS (0 ppm) or $CHCl_3$ (7.28 ppm for ^{1}H and 77.1 ppm for ^{13}C). IR were obtained on HORIBA FREEXACT-II FT-710 spectrometer. Optical rotations were recorded on a HORIBA SEPA-200 or SEPA-300 polarimeter at the sodium D line. Low-resolution mass spectra (LRMS) and High-resolution mass spectra (HRMS) were obtained on either a JOEL JMS-DX-303 or a JMS-AX-500 (EI or FAB). Optical puries were determined on a Hitachi LaChrom HPLC instrument equipped with the DAICEL chiral column.

(2*S*)-*N*-Benzyloxycarbonyl-prolinal (3): To a solution of Z-L-proline (43.4 g, 174 mmol) in DMF (200 mL) were added K_2CO_3 (121 g, 1.75 mmol) and MeI (16.2 mL, 260 mmol) at 0°C and the mixture was stirred for 2 h. To the mixture were added H_2O and Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. To the residue in THF (300 mL) was added $LiAlH_4$ (13.2 g, 348 mmol) at 0°C and the mixture was stirred for 1 h. H_2O (15 mL) and 1N NaOH (30 mL) were added and filtered. Evaporation of the solvent provided an oil, which was purified with silica gel column chromatography (hexane:AcOEt = 4:1) to give Z-prolinol (24.2 g, 103 mmol, 59%) as a colorless oil: IR (film) ν = 3410, 3033, 2954, 1684, 1415, 1358, 1105, 769, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ =

1.50-2.10 (m, 4H), 3.30-3.70 (m, 4H), 4.01 (brs, 1H), 4.32 (brs, 1H), 5.15 (s, 2H), 7.36 (m, 5H). Optical purity was determined to be 99%ee by HPLC using CHIRALCEL OD-H column (0.46 cmΦ × 25 cm); elution with 2% *i*-PrOH in hexane, t_R = 8.11 min for *S* isomer, t_R = 9.91 min for *R* isomer. To a solution of Z-prolinol (2.45 g, 10.5 mmol) in DMSO (30 mL) were added sulfur trioxide pyridine complex (5.00 g, 31.4 mmol) and Et_3N (13.9 mL, 98.8 mmol) and the mixture was stirred for 1 h. To the mixture were added H_2O, and Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 6:1) to give Z-prolinal (**3**) (1.22 g, 5.25 mmol, 51%) as a colorless oil: $[\alpha]_D^{25}$ -211.5° (*c* 0.10, $CHCl_3$); IR (film) ν = 3033, 2956, 2702, 1732, 1695, 1413, 1357, 1101, 769, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.89 (m, 2H), 2.06 (m, 2H), 3.58 (m, 2H), 4.22 (m, 0.5H), 4.33 (m, 0.5H), 5.12 (m, 2H), 7.35 (m, 5H), 9.51 (d, 0.5H, *J* = 2.4 Hz), 9.62 (d, 0.5H, *J* = 1.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.9, 24.6, 26.7, 27.9, 46.8, 47.4, 65.0, 65.4, 67.4, 128.1, 128.2, 128.62, 136.6, 200.1; MS: m/z = 234 (MH^+, 40%), 154 (70%), 91 (100%). HRMS Calcd. for $C_{13}H_{16}NO_3$: 234.1130. Fonud: 234.1125. Optical purity was determined to be 98%ee by HPLC using CHIRALCEL OJ-H column (0.46 cmΦ × 25 cm); elution with 0.5% *i*-PrOH in hexane, t_R = 22.95 min for *S* isomer, t_R = 28.64 min for *R* isomer.

(2*S*)-*N*-Benzyloxycarbonyl-2-pyrrolidinylethanal (4): To a solution of (methoxymethyl)triphenylphosphonium chloride (2.92 g, 8.50 mmol) and potassium *tert*-butoxide (960 mg, 8.50 mmol) in THF (20 mL) was added Z-prolinal (1.00 g, 4.29 mmol), and the mixture was stirred at room temperature for 30 min. To the mixture were added H_2O and Et_2O, and the organic layer was washed with brine, and dried over $MgSO_4$, and evaporated in vacuo. The product was stirred in 1N HCl-THF (1:5 mixture, 10 mL) for 30 min. The mixture was extracted with Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$. The solvent was removed, and the product was purified with silica gel column chromatography (hexane:AcOEt = 8:1) to give **4** (707 mg, 2.71 mmol, 63%) as a colorless oil, $[\alpha]_D^{25}$ +4.9° (*c* 1.22, $CHCl_3$); IR (film) ν = 3033, 2956, 2727, 1718, 1699, 1415, 1358, 1105, 769, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.89 (m, 2H), 2.16 (m, 1H), 2.53 (m, 1H), 2.97 (m, 1H), 3.46 (m, 2H), 4.34 (m, 1H), 5.14 (s, 2H), 7.36 (m, 5H), 9.69 (brs, 0.4H), 9.82 (brs, 0.6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 22.8, 23.6, 31.1, 31.9, 46.3, 46.6, 48.4, 49.1, 52.1, 52.9, 66.6, 127.7, 127.9, 128.0, 128.6, 128.8, 136.7, 154.7, 200.6; MS: m/z = 248 (MH^+, 45%), 154 (45%), 91 (100%). HRMS Calcd. for $C_{14}H_{18}NO_3$: 248.1281. Fonud: 248.1288. Optical purity was determined to be 98%ee by HPLC using chiral CHIRALCEL AD-H column (0.46 cmΦ × 25 cm); elution with 2% *i*-PrOH in hexane, t_R = 21.70 min for *S* isomer, t_R = 26.26 min for *R* isomer.

(2*S*)-*N*-Benzyloxycarbonyl-2-hydroxypropyrrolidine (5): To a solution of **4** (271 mg, 1.04 mmol) in THF (5 mL) was added methylmagnesium iodide (2M in Et_2O, 1.50 mL) at -20°C and mixture was stirred for 20 min. To the mixture were added saturated *aq*. NH_4Cl and Et_2O, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 2:1) to give **5** (205 mg, 779 μmol, 75%) as a diastereomeric mixtures. Low polar **5** as a colorless oil, $[\alpha]_D^{25}$ -6.4° (*c* 0.94, $CHCl_3$); IR (film) ν = 3438, 3033, 2966, 1699, 1684, 1356, 1105, 769, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.21 (d, 3H, *J* = 5.7 Hz), 1.48 (m, 1H), 1.72 (m 1H), 1.96 (m, 4H), 3.43 (t, 2H, *J* = 5.7 Hz), 3.88 (brs, 1H), 4.01 (m, 1H), 5.14 (s, 2H), 7.36 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.0, 23.8, 24.2, 31.1, 32.0, 45.2, 46.3, 54.6, 56.1, 66.4, 66.9, 127.9, 128.0, 128.5, 136.9, 155.6; MS: m/z = 264 (MH^+, 95%), 154 (70%), 91 (100%). HRMS Calcd. for $C_{15}H_{22}NO_3$: 264.1600. Fonud: 264.1598. High polar **5** as a colorless oil, $[\alpha]_D^{25}$ -4.2° (*c* 0.72, $CHCl_3$); IR (film) ν = 3431, 3032, 2966, 1700, 1684, 1414, 1358, 1109, 769, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.19 (d, 3H, *J* = 6.0 Hz), 1.47 (m, 2H), 1.63 (brs, 1H), 1.93 (m, 3H), 3.43 (m, 2H), 3.76 (m, 1H), 4.23 (m, 1H), 5.16 (s, 2H), 7.38 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 22.7, 23.7, 31.2, 45.6, 46.4, 54.8, 63.8, 67.2, 127.9, 128.1, 128.6, 129.0, 136.8, 157.0; MS: m/z = 264 (MH^+, 50%), 154 (100%), 91 (45%). HRMS Calcd. for $C_{15}H_{22}NO_3$: 264.1600. Fonud: 264.1600.

(2*S*)-*N*-*trans*-Cinnamoyl-2-hydroxypropyrrolidine (8): To a solution of **5** (27 mg, 102 μmol) in MeOH (5 mL) were added HCO_2NH_4 (64 mg, 1.0 mmol) and Pd-C (20 mg). The mixture was stirred for 40 min at 50°C and the solvent was removed in vacuo. The residue was added to H_2O, extracted with AcOEt, dried over $MgSO_4$, and evaporated in vacuo. To the residue in CH_2Cl_2 (2 mL) were added *trans*-cinnamic acid (20 mg, 134 μmol), HATU (58 mg, 204 μmol), HOAt (28 mg, 204 μmol), and *i*Pr_2NEt (50 μL, 703 μmol), and the mixture was stirred at room temperature for 10 h. To the mixture were added H_2O and CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 1:1) to give **8** (20 mg, 77 μmol, 75%) as a colorless oil, IR (film) ν = 3410, 2966, 1647, 1456, 1435, 1151, 843 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.18 (d, 2H, *J* = 6.1 Hz), 1.26 (d, 1H, *J* = 6.1 Hz), 1.55-2.10 (m, 6H), 3.62 (m, 2H), 3.80 (m, 1H), 4.40 (m, 1H), 6.72 (d, 1H, *J* = 15.4 Hz), 7.36 (m, 3H), 7.51 (m, 2H), 7.71 (d, 1H, *J* = 15.4 Hz); MS: m/z = 260 (MH^+, 20%), 282 (M^++Na, 100%). HRMS Calcd. for $C_{16}H_{22}NO_2$: 260.1651. Fonud: 260.1653.

(2*S*)-*N*-*trans*-Cinnamoyl-2-oxoxypropyrrolidine (*trans*-dendrochrysanine; 1): To a solution of **8** (20 mg, 77 μmol) in acetone (2 mL) was added Jones' reagent at 0°C and the mixture was stirred for 20 min. To the mixture were added isopropanol and Et_2O, and the organic layer was washed with brine, dried over

$MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 1:1) to give **1** (19 mg, 73 μmol, 95%) as a colorless oil, $[\alpha]_D^{25}$ -11.8° (*c* 0.15, $CHCl_3$); IR (film) ν = 2930, 1711, 1649, 1601, 1419, 1149, 980, 766 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 1.78 (m, 1H), 2.00 (m, 2H), 2.14 (m ,2H), 2.21 (s, 3H), 2.49 (dd, 1H, *J* = 16.6, 9.5 Hz), 3.28 (dd, 1H, *J* = 12.0, 7.8 Hz), 3.67 (m 2H), 4.54 (m, 1H), 6.73 (d, 1H, *J* = 15.6 Hz), 7.39 (m, 3H), 7.54 (m, 2H), 7.70 (d, 1H, *J* = 15.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 23.7, 29.9, 30.0, 46.7, 46.8, 53.6, 118.7, 127.6, 128.5, 129.4, 134.9, 141.7, 164.5; MS: m/z = 131 (100%), 257 (M^+, 30%). HRMS Calcd. for $C_{16}H_{19}NO_2$: 257.1416. Fonud: 257.1414.

(2*S*)-*N*-*cis*-Cinnamoyl-2-hydroxypropyrrolidine (9): To a solution of **6** (15 mg, 116 μmol) in CH_2Cl_2 (1 mL) were added *cis*-cinnamic acid (18 mg, 121 μmol), PyBOP (60 mg, 115 μmol), and *i*Pr_2NEt (50 μL, 703 μmol). The mixture was stirred at room temperature for 10 h. To the mixture were added H_2O and CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 1:1) to give **11** (23 mg, 87 μmol, 75%) as a colorless oil, $[\alpha]_D^{25}$ -20.0° (*c* 0.20, $CHCl_3$); IR (film) ν = 2923, 1712, 1612, 1434, 1371, 1153, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.56 (m, 1H), 1.73 (m, 2H), 2.07 (m, 1H), 2.19 (s, 3H), 2.38 (dd, 1H, *J* = 16.5, 9.6 Hz), 3.12 (td, 1H, *J* = 10.8, 6.6 Hz), 3.31 (m, 2H), 4.43 (m, 1H), 6.03 (d, 1H, *J* = 12.6 Hz), 6.65 (d, 1H, *J* = 12.6 Hz), 7.30 (m, 3H), 7.40 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 24.0, 30.2, 30.7, 46.6, 47.4, 53.3, 124.3, 128.38, 128.44, 128.6, 123.9, 135.7, 162.4, 207.0; MS: m/z = 260 (MH^+, 20%), 282 (M^++Na, 100%). HRMS Calcd. for $C_{16}H_{22}NO_2$: 260.1651. Fonud: 260.1653.

(2*S*)-*N*-*cis*-Cinnamoyl-2-oxoxypropyrrolidine (*cis*-dendrochrysanine; 2): To a solution of **9** (11 mg, 42 mmol) in CH_2Cl_2 (1 mL) was added Dess-Martin periodinane (0.2 M in CH_2Cl_2, 200 μL) at 0°C and the mixture was stirred for 20 min at 0°C. To the mixture were added H_2O and CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The product was purified with silica gel column chromatography (hexane:AcOEt = 1:1) to give **2** (8 mg, 31 mmol, 73%) as a colorless oil, $[\alpha]_D^{25}$ -14.5° (*c* 0.04, $CHCl_3$); IR (film) n = 2923, 1712, 1612, 1434, 1371, 1153, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) d = 1.56 (m, 1H), 1.73 (m, 2H), 2.07 (m, 1H), 2.19 (s, 3H), 2.38 (dd, 1H, *J* = 16.5, 9.6 Hz), 3.12 (td, 1H, *J* = 10.8, 6.6 Hz), 3.31 (m, 2H), 4.43 (m, 1H), 6.03 (d, 1H, *J* = 12.6 Hz), 6.65 (d, 1H, *J* = 12.6 Hz), 7.30 (m, 3H), 7.40 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) d = 24.0, 30.2, 30.7, 46.6, 47.4, 53.3, 124.3, 128.38, 128.44, 128.6, 123.9, 135.7, 162.4, 207.0; FABMS: m/z = 258 (MH^+, 45%), 69 (100%). HRMS Calcd. for $C_{16}H_{20}NO_2$: 258.1494. Fonud: 258.1498.

ACKNOWLEDGEMENTS

We thank Prof. Nobutaka Fujii and Dr. Shinya Oishi of the Graduate School of Pharmaceutical Sciences, Kyoto University for the measurements of NMR and MS spectra, and Prof. Shigefumi Kuwahara and Mr. Takashi Nakahata of the Graduate School of Agriculture, Tohoku University for the measurements of optical rotation and CD spectra.

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