Synthetic Studies on Quassinoids: Synthesis of (±)-Shinjudilactone and (±)-13-*epi*-Shinjudilactone

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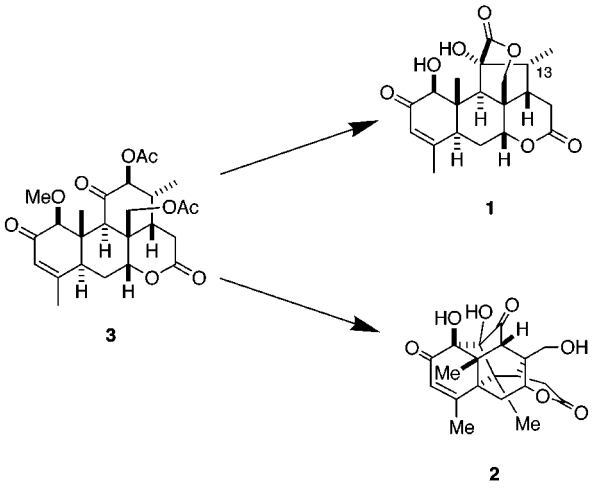
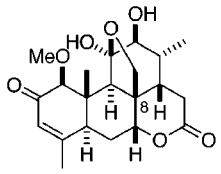
During the course of examining the bitter principles of *Ailanthus altissima* Swingle, two novel quassinoids, shinjudilactone (**1**) and shinjulactone C (**2**), possessing modified picrasane skeletons, were isolated and characterized.[1] We have on a previous occasion reported on the total synthesis of (±)-shinjulactone C (**2**) which proceeded via the intermediacy of tetracyclic lactone **3**.[2] We detail below the transformation of **3** into (±)-shinjudilactone (**1**) which constitutes a total synthesis of (±)-**1**.[3] The synthesis features a benzilic acid-like rearrangement which leads directly to (±)-**1** and (±)-13-*epi*-shinjudilactone.

Initial efforts to transform **3** into **1** centered around converting synthetic (±)-**3** into hemiketal **4** so as to permit exclusive oxidation at C(12). It was anticipated



3 **1** **2**

that exposure of **5** to benzilic acid-like rearrangement conditions would lead to migration of C(9) from C(11) to C(12) with formation of C(1) *O*-methyl shinjudilactone **6**. Demethylation would afford (±)-shinjudilactone (**1**). Thus, hydrolysis of the acetates in **3** with potassium carbonate in a methanol−dichloromethane mixture gave rise to an 82% isolated yield of crystalline **4**, mp 248−250 °C. Note that one cannot isolate the diol containing the C(8) hydroxymethyl group since ring closure to the hemiketal is instantaneous and complete. Oxidation (Swern conditions) at C(12) furnished pentacyclic enedione **5**, mp 238.5−240.0 °C, in 70% yield. All efforts to induce **5** to undergo a benzilic acid-like rearrangement under a variety of acidic (hydrochloric acid, acetic acid, boron trifluoride etherate) and basic conditions (sodium bicarbonate or lithium hydroxide in aqueous methanol at elevated temperatures, barium hydroxide in pyridine) failed to generate even a trace of **6**. Workup provided recovered starting material and extensive decomposition products which could not be characterized.



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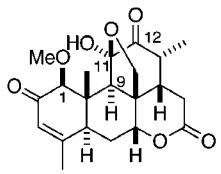

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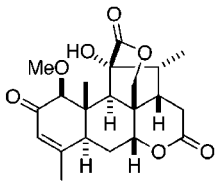

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In the event that the C(1) *O*-methyl group in enedione **5** was in some way responsible for the unsuccessful attempts to transform **5** into **6**, we set out to prepare **9** which would provide another opportunity to bring about the required benzilic acid-like rearrangement with, in this case, direct formation of (±)-shinjudilactone (**1**). There was considerable concern that the sensitive nature of the ring A 1β-hydroxy-2-oxo-$\Delta^{3,4}$ olefin array would not be compatible with the conditions required to effect rearrangement. Nonetheless, compound **3** was subjected to demethylation (BBr_3, CH_2Cl_2, −45 °C) giving rise to hydroxy enedione **7**, mp 249−250 °C, in 71% yield along with ca. 11% recovered **3**. Hydrolysis of the acetates in **7** utilizing potassium carbonate in a methanol−dichloromethane mixture provided pentacyclic compound **8**, mp 235−237 °C, in 95% yield. It was anticipated based on previous work on quassinoids in our laboratory[4] that the hindered nature of the C(1) hydroxyl group would permit selective oxidation at C(12). Accordingly, oxidation of **8** employing carefully controlled Swern conditions gave rise to the key pentacyclic dione **9**, mp 188.5−191.0 °C, in 56% yield along with 17% of recovered **8** which could be recycled.

With substrate **9** in hand, efforts were focused on the benzilic acid-like rearrangement. Exposure (30 min) of **9** to sodium bicarbonate in 50% aqueous methanol at 95 °C gave rise (60%) to a 1:1 mixture of (±)-shinjudilactone (**1**) and (±)-13-*epi*-shinjudilactone (**10**), both highly crystalline compounds, which were readily separated by preparative TLC. The structures initially assigned to shinjudilactone and *epi*-shinjudilactone were based on a comparison of their respective ^1H and ^{13}C NMR spectra with those of **1** and **10** reported[1] in the literature. Unable to obtain authentic samples of (+)-**1** and (+)-**10** for direct

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(1) Ishibashi, M.; Tsuyuki, T.; Murae, T.; Hiroto, H.; Takahashi, T.; Itai, A.; Iitaka, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3683.

(2) Collins, J. L.; Grieco, P. A.; Gross, R. S. *J. Org. Chem.* **1990**, *55*, 5816.

(3) For the conversion of natural ailanthone into (+)-shinjudilactone and (+)-13-*epi*-shinjudilactone, see ref 1.

(4) Grieco, P. A.; Collins, J. L.; Moher, E. D.; Fleck, T. J.; Gross, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 6078.

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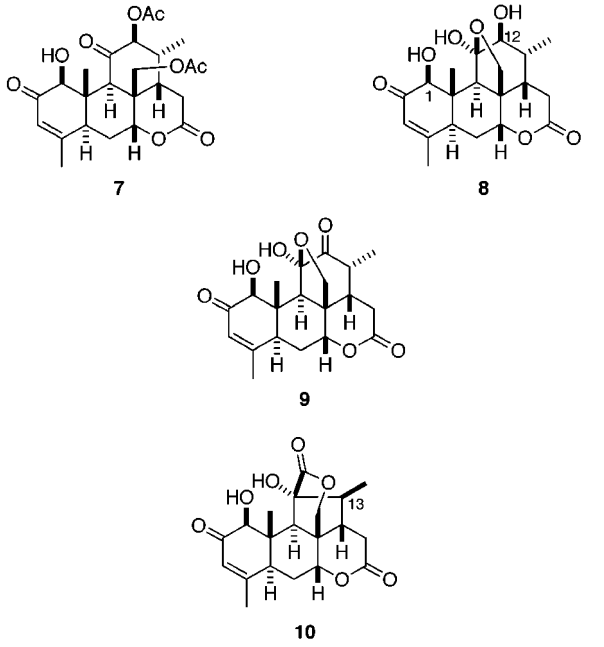

comparison, the compound assumed to be (±)-shinjudilactone, based on the NMR data in the literature, was subjected to single-crystal X-ray analysis.[5] Much to our surprise, the crystal structure obtained was that of (±)-*epi*-shinjudilactone (**10**). An ORTEP stereoview of **10** is shown in Figure 1. Having unambiguously established the structure of (±)-*epi*-shinjudilactone (**10**), one can only conclude that the NMR spectra in the literature for **1** and **10** must have been inadvertently switched during tabulation. For a comparison of the ^{13}C NMR data for our synthetic **1** and **10** with the uncorrected data in the literature, see Table 1.

Experimental Section[6]

(1*β*,11*β*,12*β*)-11,12-Dihydroxy-11,20-epoxy-1-methoxypicras-3-ene-2,16-dione (4). A solution of 81 mg (0.17 mmol) of diacetate **3** dissolved in 4 mL of methanol and 3 mL of dichloromethane at room temperature under argon was treated with 49 mg (0.36 mmol) of potassium carbonate. After stirring for 3.3 h, the reaction mixture was acidified with 4 drops of a 10% aqueous hydrochloric acid solution, filtered through a pad of flash silica gel, and concentrated in vacuo. The crude product was chromatographed on 15 g of flash silica gel. Elution with chloroform−methanol (93:7) provided 55 mg (82%) of hemiketal **4** as a white solid: R_f 0.35 (chloroform-methanol, 9:1); IR ($CHCl_3$) 3500 (m), 3260 (m), 1730 (s), 1689 (s), 1665 (s), 1620 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$−MeOH-d_4/95:5) δ 5.96 (m, 1H), 4.46 (t, J = 2.7 Hz, 1H), 3.93 (d, J = 8.8 Hz, 1H), 3.65 (d, J = 8.8 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 1H), 3.10 (d, J = 9.5 Hz, 1H), 2.80−2.64 (m, 2H), 2.34 (dd, J = 18.8, 13.5 Hz, 1H), 2.19 (dt, J = 14.8, 2.7 Hz, 1H), 2.13−2.00 (m, 2H), 1.98−1.86 (m, 1H), 1.91 (br s, 3H), 1.84 (s, 1H), 1.20 (s, 3H), 1.02 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$−MeOH-d_4/95:5) δ 195.42, 170.02, 160.66, 126.68, 106.39, 92.80, 79.46, 77.87, 71.48, 60.95, 49.06, 46.04, 44.64, 42.42, 42.07, 34.14, 28.88, 25.35, 22.37, 13.38, 10.15; high-resolution MS (CI) calcd for $C_{21}H_{29}O_7$ (M + 1) *m/e* 393.1913, found 393.1913; calcd for $C_{21}H_{28}O_7$ (*M*) *m/e* 392.1835, found 392.1837. An analytical sample was prepared by recrystallization from acetone, mp 248−250

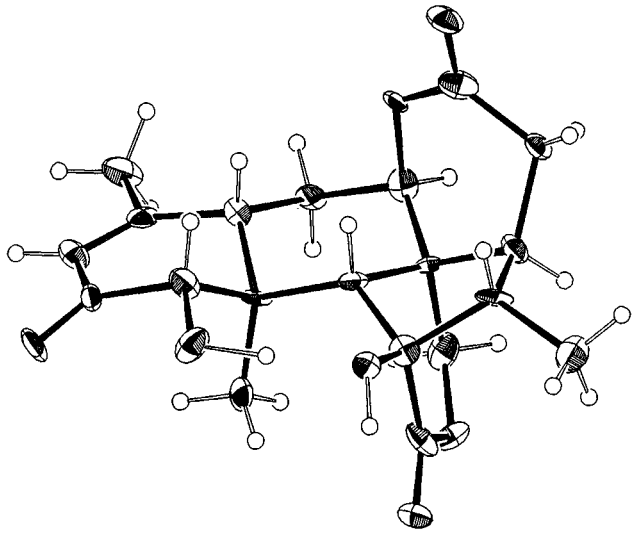

Figure 1. ORTEP stereoview of (±)-**10**.

Table 1. ^{13}C NMR Data[a]

carbon number	reported for (+)-**1**[1]	found for (±)-**1**	reported for (+)-**10**[1]	found for (±)-**10**
1	83.5	83.5	83.8	83.8
2	196.7	196.9	196.9	197.0
3	126.3	126.4	126.3	126.4
4	161.8	161.8	162.0	162.0
5	41.9	41.9	42.2	42.2
6	27.0	27.0	27.0	26.9
7	74.3	74.3	73.9	73.9
8	44.5	44.5	48.4	48.4
9	51.0	50.9	55.0	55.0
10	42.5	42.5	43.0	43.0
11	76.6	76.6	78.7	79.0
12	175.7	175.8	173.5	173.5
13	42.8	42.8	45.6	45.6
14	48.3	48.3	53.6	53.6
15	29.3	29.3	32.9	32.9
16	170.9	171.0	170.6	170.6
17	22.2	22.2	22.1	22.1
18	9.8	9.8	10.6	10.6
19	76.0	76.0	76.2	76.2
20	11.4	11.4	13.8	13.8

[a] Note that in ref 1 the ^{13}C NMR data for (+)-**1** and (+)-**10** were inadvertently switched and incorrectly tabulated.

(5) (±)-13-*epi*-Shinjudilactone (**10**) crystallizes in space group $P2_1/n$ with cell dimensions (at −172 °C) of a = 7.833(4) Å, b = 18.244(9) Å, c = 12.358(7) Å, β = 106.67(3) Å, and Z = 4. The volume of the crystral was 1691.80 Å^3 with a density of 1.478 g cm^{-3}. A total of 2950 reflections were measured, of which 1218 were determined to be observable, $F_o > 2.33\sigma(F_o)$. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. For more information, contact Dr. John C. Huffman, Indiana University, Department of Chemistry, Molecular Structure Center, Bloomington, IN 47405, Report No. 90302.

(6) Proton and carbon nuclear magnetic resonance spectra were recorded on a Varian VXR-400 MHz or a Bruker DPX 300 MHz spectrometer. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (δ 0.0). Infrared (IR) spectra were taken on a Perkin-Elmer model 298 spectrophotometer, a Mattson Galaxy 4020 series FTIR spectrometer, or on a Perkin-Elmer model 1600 FTIR. Absorption intensities are indicated as strong (s), medium (m), or weak (w). High-resolution mass spectra were obtained on a VG Instruments 70E-HF mass spectrometer. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ). Melting points were obtained on a Fisher-Johns hot-stage or on a MEL-TEMP capillary melting point apparatus and are uncorrected. Optical rotations were obtained on a Perkin-Elmer model 241 polarimeter. Reactions were monitored by thin-layer chromatography (TLC) using E. Merck precoated silica gel 60 F-254 (0.25 mm) plates. E. Merck precoated silica gel 60 F-254(0.50 mm) plates were used for preparative plate chromatography. E. Merck silica gel 60(230−400 mesh) was used for flash chromatography.

°C. Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.15; H, 7.11.

(1*β*,11*β*)-11,20-Epoxy-11-hydroxy-1-methoxypicras-3-ene-2,12,16-trione (5). A solution of 98 μL (1.38 mmol) of anhydrous dimethyl sulfoxide dissolved in 2.7 mL of anhydrous dichloromethane at −78 °C under argon was treated dropwise with 60 μL (0.69 mmol) of oxalyl chloride. After stirring at −78 °C for 20 min, 54 mg (0.14 mmol) of alcohol **4** dissolved in 1.8 mL of anhydrous dichloromethane was added dropwise over 3 min. The reaction was stirred at −78 °C for 5 min then warmed to −23 °C and stirred for 15 min. Upon cooling to −78 °C, 191 μL (1.38 mmol) of anhydrous triethylamine was added dropwise. After stirring at −78 °C for 5 min then at 0 °C for 25 min, the reaction mixture was poured into 15 mL of a saturated aqueous sodium bicarbonate solution, and the layers were separated. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude residue was chromatographed on 25 g of flash silica gel. Elution with chloroform−methanol (95:5) provided 38 mg (70%) of ketone **5** as a white solid: R_f 0.35 (chloroform−methanol, 95:5); IR ($CHCl_3$) 3520 (w), 3245 (m), 1733 (s), 1689 (s), 1630 (w) cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 8.00 (br s, 1H), 5.99 (m, 1H), 4.74 (t, J = 2.8 Hz, 1H), 4.39 (d, J = 9.0 Hz, 1H), 4.11 (d, J = 9.0 Hz, 1H), 3.95 (s, 1H), 3.60 (s, 3H), 3.47−3.37 (m, 1H), 3.04 (br d, J = 12.4 Hz, 1H), 2.83−2.70 (m, 2H), 2.70−2.58 (m, 1H), 2.65 (s, 1H), 2.21 (dt, J = 15.2, 2.8 Hz, 1H), 2.10−2.00 (m, 1H), 1.72 (br s, 3H), 1.49 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, C_5D_5N) δ 207.49, 195.58, 169.13, 160.71, 127.15, 108.02, 92.85, 77.35, 72.84, 60.65, 51.11, 46.77, 45.45, 43.46, 42.75, 40.62, 28.68, 25.83, 22.16, 10.71, 10.18; high-resolution MS (CI) calcd for $C_{21}H_{27}O_7$ (M + 1) *m/e* 391.1757, found 391.1752. An analytical sample was prepared by recrystallization from acetone, mp 238.5−240 °C. Anal. Calcd for $C_{21}H_{26}O_7$: C, 64.60; H, 6.71. Found: C, 64.57; H, 6.68.

(1*β*,12*β*)-12,20-Bis(acetyloxy)-1-hydroxypicras-3-ene-2,11,16-trione (7). To a solution of 50 mg (0.105 mmol) of methyl ether **3** dissolved in 3.7 mL of anhydrous dichloromethane at −23 °C was added in dropwise fashion 1.05 mL (1.05 mmol) of a 1.0 M solution of boron tribromide in dichloromethane. After stirring for 30 min, the reaction was transferred *via cannula* into a cold (0 °C) saturated aqueous sodium bicarbonate solution (6 mL). After stirring for 10 min, the reaction contents were diluted with dichloromethane and water. The aqueous layer was extracted with dichloromethane and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The residue was purified on 30 g of flash silica gel. Elution with ethyl acetate−hexanes (8:2) provided 5.6 mg (11%) of recovered **3** and 44 mg (71%) of alcohol **7** as a white solid: R_f 0.21 (chloroform−methanol, 95:5); IR ($CHCl_3$) 3480 (w), 1740 (s), 1677 (s) 1620 (w) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.07 (m, 1H), 5.02 (d, J = 12.0 Hz, 1H), 4.64 (d, J = 12.9 Hz, 1H), 3.90 (d, J = 12.9 Hz, 1H), 4.62 (t, J = 3.1 Hz, 1H), 3.90 (d, J = 2.5 Hz, 1H), 3.83 (d, J = 2.5 Hz, 1H), 3.07 (s, 1H), 2.93 (dd, J = 18.9, 7.0 Hz, 1H), 2.82 (br d, J = 12.7 Hz, 1H), 2.80 (dd, J = 18.9, 12.9 Hz, 1H), 2.69−2.61 (m, 1H), 2.49−2.39 (m, 1H), 2.23 (dt, J = 15.0, 3.1 Hz, 1H), 2.18 (s, 3H), 2.10 (s, 3H), 2.09−2.00 (m, 1H), 1.96 (br s, 3H), 1.23 (s, 3H), 1.09 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, C_5D_5N) δ 200.03, 196.78, 170.05, 169.79, 168.44, 162.07, 125.17, 84.46, 78.19, 77.73, 61.41, 50.59, 45.57, 43.39, 41.91, 36.34, 35.87, 27.01, 25.06, 22.34, 20.69, 20.49, 14.85, 10.55. An analytical sample was prepared by recrystallization from acetone, mp 249−250 °C. Anal. Calcd for $C_{24}H_{30}O_9$: C, 62.33; H, 6.54. Found: C, 62.53; H, 6.64.

(1*β*,11*β*,12*β*)-1,11,12-Trihydroxy-11,20-epoxypicras-3-ene-2,16-dione (8). To a solution of 25 mg (0.054 mmol) of diacetate **7** dissolved in 1.3 mL of anhydrous methanol and 650 μL of anhydrous dichloromethane at ambient temperature under argon was added 15 mg (0.11 mmol) of potassium carbonate. After being stirred for 70 min, the reaction contents were acidified with 2 drops of a 10% aqueous hydrochloric acid solution, filtered through silica gel, and washed with chloroform−methanol (9:1). The filtrate was concentrated in vacuo and the crude residue was chromatographed on two silica gel analytical TLC plates (0.25 mm thickness). Elution with chloroform−methanol (93:7) provided 19 mg (95%) of hemiketal **8** as a white solid: R_f 0.30 (chloroform−methanol, 9:1); IR (KBr) 3553 (s), 3356 (m), 1721 (s), 1658 (s), 1612 (w) cm^{-1}; ^{1}H NMR (500 MHz, C_5D_5N) δ 6.07 (br s, 1H), 4.56 (br s, 1H), 4.41 (s, 1H), 4.11 (d, J = 8.6 Hz, 1H), 3.77 (d, J = 8.6 Hz, 1H), 3.67 (d, J = 10.1 Hz, 1H), 2.96−2.81 (m, 3H), 2.62 (s, 1H), 2.46−2.36 (m, 1H), 2.15 (br d, J = 14.5 Hz, 1H), 2.07 (dt, J = 13.3, 6.7 Hz, 1H), 2.01−1.92 (m, 1H), 1.70 (br s, 3H), 1.51 (s, 3H), 1.17 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, C_5D_5N) δ 197.19, 170.13, 161.77, 126.28, 108.38, 84.72, 79.85, 78.32, 72.07, 49.74, 46.49, 45.77, 42.56, 42.24, 35.34, 29.53, 26.10, 22.33, 14.11, 10.42. An analytical sample was prepared by recrystallization from chloroform−methanol (9:1), mp 235−237 °C. Anal. Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93. Found: C, 63.26; H, 6.90.

(1*β*,11*β*)-1,11-Dihydroxy-11,20-epoxypicras-3-ene-2,12,16-trione (9). A solution of 7 μL (0.095 mmol) of anhydrous dimethyl sulfoxide dissolved in 200 μL of anhydrous dichloromethane at −78 °C under argon was treated dropwise with 4 μL (0.048 mmol) of anhy-drous oxalyl chloride. After stirring at −78 °C for 15 min, 18 mg (0.048 mmol) of alcohol **8** dissolved in 500 μL of anhydrous dichloromethane and 400 μL of anhydrous dimethyl sulfoxide was added in a dropwise fashion. The reaction was stirred at −78 °C for 10 min then warmed to −23 °C and stirred for 20 min. Upon cooling to −78 °C, 13 μL (0.095 mmol) of anhydrous triethylamine was added dropwise. After stirring at −78 °C for 5 min then at 0 °C for 20 min, the reaction mixture was filtered through a pad of silica gel. The filtrate was concentrated in vacuo, and the crude residue was chromatographed on a silica gel analytical TLC plate (0.25 mm thickness). Elution with chloroform-methanol (95:5) provided 3.0 mg (17%) of recovered **8** and 10 mg (56%) of ketone **9** as a white solid. R_f 0.37 (chloroform−methanol, 9:1); IR (KBr) 3401 (w), 1726 (s), 1676 (s), 1624 (w) cm^{-1}; ^{1}H NMR (500 MHz, C_5D_5N) δ 6.06 (br s, 1H), 4.77 (br s, 1H), 4.44 (d, J = 8.8 Hz, 1H), 4.13 (d, J = 8.8 Hz, 1H), 4.41 (s, 1H), 3.47−3.39 (m, 1H), 3.00 (br d, J = 12.6 Hz, 1H), 2.90 (s, 1H), 2.86−2.71 (m, 2H), 2.66−2.58 (m, 1H), 2.23 (dt, J = 14.8, 2.0 Hz, 1H), 2.13−2.04 (m, 1H), 1.71 (br s, 3H), 1.57 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H); high-resolution MS (EI) calcd for $C_{20}H_{24}O_7$ (M) *m/e* 376.1522, found 376.1528; calcd for $C_{20}H_{22}O_6$ (M − H_2O) *m/e* 358.1417, found 358.1411. An analytical sample was prepared by recrystallization from acetone, mp 188.5−191 °C. Anal. Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.69; H, 6.39.

(±)-Shinjudilactone (1) and (±)-13-*epi*-Shinjudilactone (10). A heterogeneous mixture of 27 mg (0.071 mmol) of ketone **9** in 3.38 mL of water and 3.38 mL of methanol was treated with 16.9 mg (0.201 mmol) of sodium bicarbonate. The reaction was heated to 95 °C and stirred for 30 min. Upon cooling to ambient temperature, the reaction was acidified with 5 drops of a 10% aqueous hydrochloric acid solution and concentrated to ca. 3 mL. The residue was extracted with chloroform and the combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to a yellow solid. The residue was chromatographed on analytical silica gel TLC plates (0.5 mm thickness). Elution with chloroform−methanol (93.5:6.5) provided 6 mg (30%) of (±)-13-*epi*-shinjudilactone **(10)** as a white solid: R_f 0.46 (chloroform−methanol, 95:5); IR (KBr) 3460 (w), 3338 (s), 1745 (s), 1664 (s), 1620 (w) cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 6.07 (br s, 1H), 4.76 (d, J = 11.4 Hz, 1H), 4.24 (d, J = 11.4 Hz, 1H), 4.75 (br s, 1H), 4.20 (s, 1H), 3.21 (br d, J = 12.9 Hz, 1H), 3.08 (dd, J = 16.4, 10.2 Hz, 1H), 2.72 (s, 1H), 2.69 (d, J = 16.4 Hz, 1H), 2.31−2.22 (m, 2H), 2.21−2.13 (m, 1H), 2.04 (t, J = 13.8 Hz, 1H), 1.76 (br s, 3H), 1.23 (d, J = 6.6 Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, C_5D_5N) δ 196.95, 173.53, 170.62, 161.97, 126.35, 83.80, 78.69, 76.18, 73.92, 54.98, 53.55, 48.35, 45.62, 42.97, 42.22, 32.88, 26.93, 22.05, 13.81, 10.57; high-resolution MS (EI) calcd for $C_{20}H_{24}O_7$ (M) *m*/*e* 376.1520, found 376.1510. An analytical sample was prepared by recrystallization from methanol−ethyl acetate, mp 245−247 °C. Anal. Calcd for $C_{20}H_{24}O_7$; C, 63.82; H, 6.43. Found: C, 63.59; H, 6.40.

In addition, 6.3 mg (33%) of (±)-shinjudilactone **(1)** was obtained as a white solid: R_f 0.42 (chloroform−methanol, 95:5); IR (KBr) 3274 (w), 1749 (s), 1672 (s), 1617 (m) cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 6.08 (br s, 1H), 5.60 (s, 1H, OH), 4.94 (s, 1H, OH), 4.71 (d, J = 11.6 Hz, 1H), 4.28 (d, J = 11.6 Hz, 1H), 4.67 (br s, 1H), 4.26 (s, 1H), 3.15 (br d, J = 14.4 Hz, 1H), 2.92−2.72 (m, 4H), 2.76 (s, 1H), 2.26 (dt, J = 14.4, 3.4 Hz, 1H), 2.06 (dt, J = 14.4, 2.4 Hz, 1H), 1.76 (br s, 3H), 1.22 (s, 3H), 1.20 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, C_5D_5N) δ 196.85, 175.76, 171.00, 161.78, 126.35, 83.50, 76.57, 75.97, 74.26, 50.90, 48.32, 44.48, 42.80, 42.45, 41.90, 29.30, 26.97, 22.16, 11.44, 9.78; high-resolution MS (EI) calcd for $C_{20}H_{24}O_7$ (M) *m*/*e* 376.1520, found 376.1506; calcd for $C_{20}H_{22}O_6$ (M − H_2O) *m*/*e* 358.1416, found 358.1416. An analytical sample was prepared by recrystallization from methanol, mp 234−236 °C. Anal. Calcd for $C_{20}H_{24}O_7$: C, 63.82; H, 6.43. Found: C, 63.64; H, 6.37.

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Supporting Information Available: Full crystallographic tables for (±)-**10** (MSC 90302) (13 pages).This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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