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Enantioselective total synthesis of hydramicromelin B

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Abstract—The first total synthesis of hydramicromelin B is described. An $AuCl_3$/AgOTf-catalyzed intramolecular reaction was used as key step for the construction the coumarin ring.

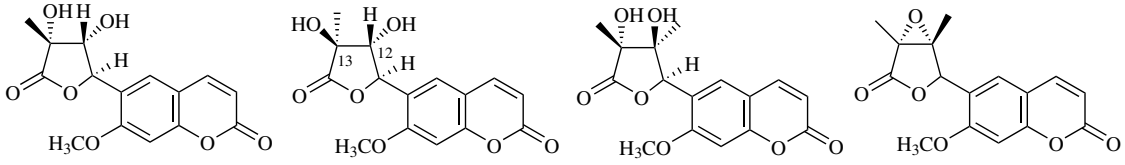
1. Introduction

Micromelin **4**, a product with a skeleton of coumarin, was first isolated by Price[1] in 1966. It showed significant inhibition against leukemia p-338 cell line (T/C 149% at 10 mg/kg) and excellent activity against Lewis lung carcinoma (T/C 228% at 1.25 mg/kg).[2] Recently, three new derivatives of micromelin, hydramicromelins **A**–**C** **1**–**3**, were isolated from the aerial part of *M. Integerrimum* and the relative configurations established by Hao[2] (Fig. 1). Hydramicromelins A–C process a coumarin ring and a five-membered lactone ring. Their significant biological activities and unique structures inspired us to achieve their total synthesis. Herein, we describe the first enantioselective synthesis and establish the absolute configuration of hydramicromelin B.

The retrosynthetic analysis is depicted in Scheme 1. Construction of the coumarin ring was envisioned via an $AuCl_3$/AgOTf-catalyzed coupling reaction of **5**. The five-membered lactone ring of **5** could be generated by the removal of all protecting groups and spontaneous ring closure of **6** under acidic conditions. A few functional group transformations would provide **6** from α,β-unsaturated ester **7**, which would be derived from aldehyde **8** and known ylide **9** via by a Wittig–Horner–Emmons (WHE) reaction.

2. Results and discussion

Our synthetic strategy is outlined in Scheme 2. The diol compound **11** was prepared from 2,4-dihydroxybenzaldehyde **10** via a four-step synthesis including selective protection of hydroxyls at the *para* and *ortho* position, Wittig olefination and dihydroxylation of the corresponding olefin in 80% overall yield.[3] Monoprotection of the primary hydroxyl group of **11** with TBSCl gave alcohol **12** in 95% yield and its enantiomeric purity was determined as 99%



Hydramicromelin A **1** Hydramicromelin B **2** Hydramicromelin C **3** Micromelin **4**

Figure 1.

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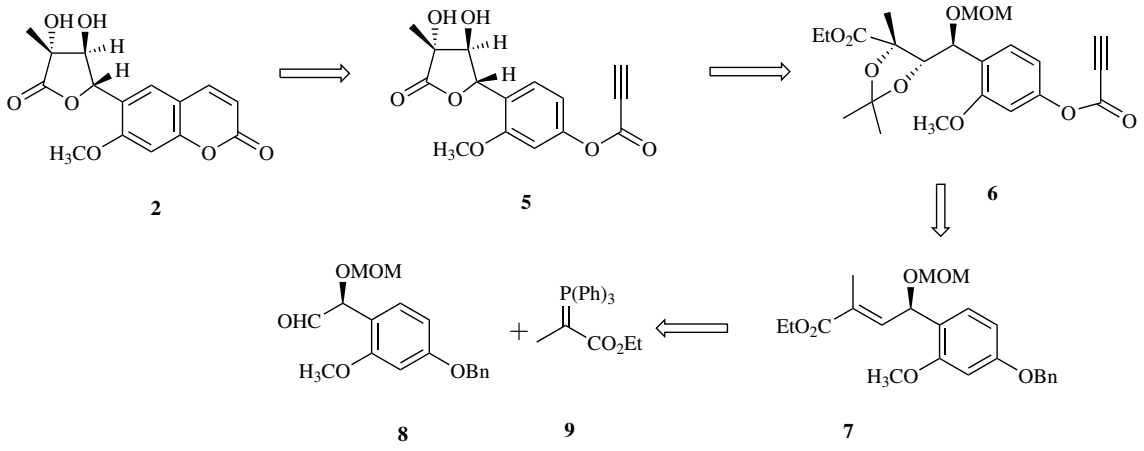
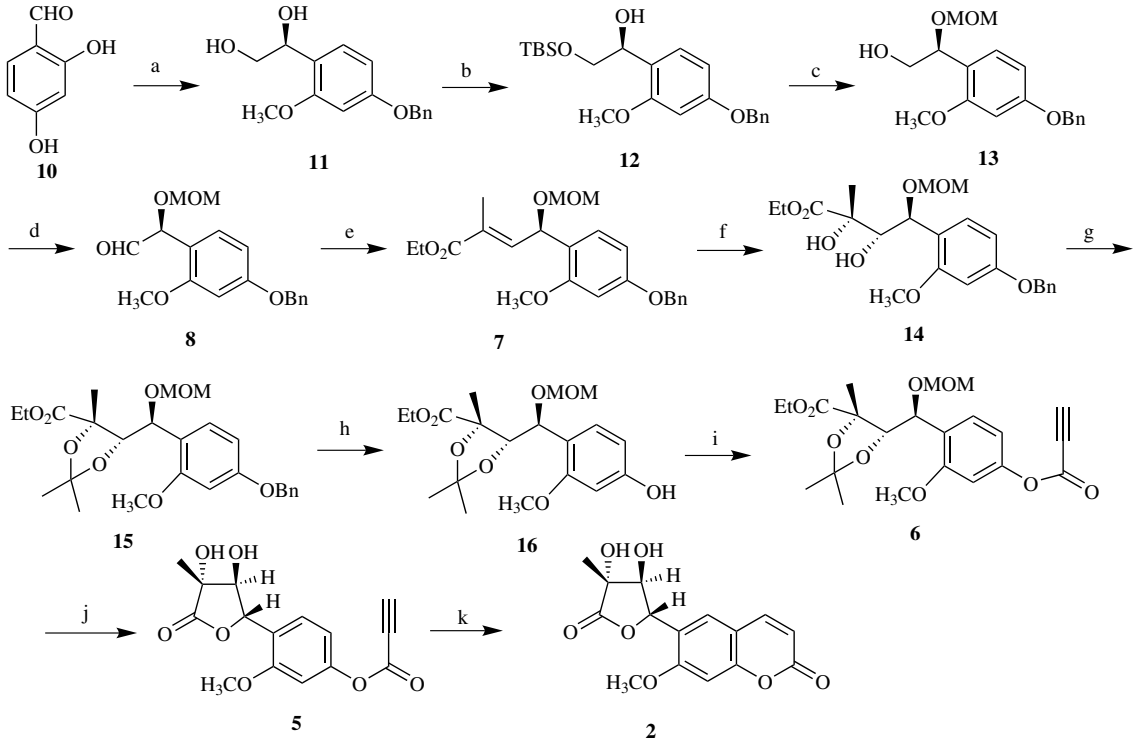


Scheme 1.



Scheme 2. Reagents and conditions: (a) (i) $NaHCO_3$, BnBr, CH_3CN, 80 °C; (ii) Me_2SO_4, K_2CO_3, acetone, rt; (iii) Ph_3PCH_3I, *n*-BuLi, THF, 0 °C; (iv) AD-mix-α, *t*-BuOH–H_2O = 1:1, 0 °C, 80% in four steps; (b) imidozole, TBSCl, CH_2Cl_2, 0 °C, 95%; (c) (i) *i*-Pr_2NEt, MOMCl, CH_2Cl_2, reflux; (ii) TBAF, THF, rt, 90% in two steps; (d) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C, 88%; (e) $Ph_3P{=}CH(Me)CO_2Et$, toluene, 80 °C, 98%; (f) OsO_4, NMO, THF–H_2O = 3:1, rt, dr = 6:1, 70%; (g) 2,2-dimethoxypropane, 10% PPTS, CH_2Cl_2, 60 °C, 83%; (h) Raney-Ni, H_2, ethanol–methanol = 4:1, 90%; (i) propiolic acid, DMAP, DCC, CH_2Cl_2, 70%; (j) THF–HCl = 4:1, rt, 70%; (k) $AuCl_3$, 5 mol %; AgOTf, 15 mol %; $ClCH_2CH_2Cl$, rt, 50%.

ee by chiral HPLC analysis. After protection of the secondary alcohol as its methoxy methyl ether (MOM), the TBS group was deprotected with tetrabutyl ammonium fluoride (TBAF) to provide the primary alcohol **13** in overall 90% yield in two steps. A combination of Swern oxidation[4] and Wittig–Horner–Emmons reaction delivered the trisubstituted *E*-olefin **7** as a single isomer from **13** in 87% yield.

Dihydroxylation of α,β-unsaturated ester **7** gave the desired diol **14** with 6:1 diastereoselectivity[5] in 70% yield. After careful purification by flash chromatography, **14** was treated with 2,2-methoxypropane[6] to afford acetonide **15**. Removal of the benzyl group with Raney-Ni resulted in the formation of phenol **16** in 72% overall yield for two steps. Acylation of hydroxyl of **16** in the presence of DCC and DMAP produced ester **6** in 70% yield,[7] and the stereochemical structure of **6** was determined by single-crystal X-ray analysis as shown in Figure 2.[8] Deprotection of MOM, deacetonization and lactonization of compound **6** in THF–HCl provided **5**. With the key intermediate **5** in

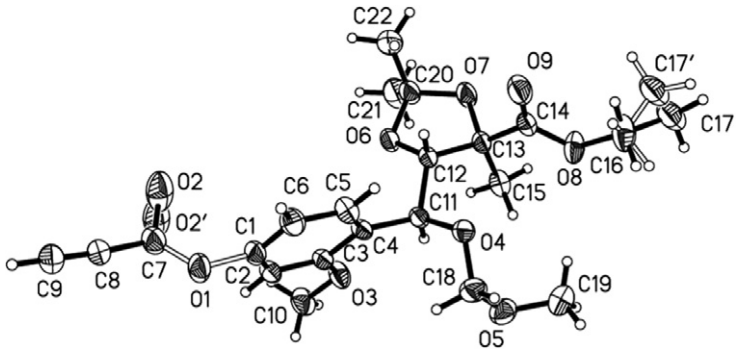


Figure 2. X-ray crystallography of **6**.

hand, after many trials,[9,10] we eventually discovered a efficient hydroarylation reaction of the alkyne and alkene to form C–C bonds.[11] It was proposed that an arygold(III) species was likely generated from electrophilic metallation of the aryl ring by $AuCl_3$. Then, the arygold(III) was added to propiotic ester to give the 1,4-addition product. The reaction catalyzed by $AuCl_3$/AgOTf under mild conditions in dichloroethane gave the desired target molecule **2** in 50% yield. Synthetic **2** exhibited ^1H, ^{13}C NMR spectral data and specific rotation was identical to those published for the natural product.[2]

3. Conclusion

In summary, the first total synthesis of hydramicromelin B **2** has been achieved within 16 steps in 7.5% overall yield. The absolute stereochemistry at C **11**, C **12** and C **13** are (*S*)-, (*S*)- and (*R*), respectively, so we established the absolute configuration of hydramicromelin B. Construction of the coumarin ring with $AuCl_3$/AgOTf catalyst system was reported for the first time in this type of natural products synthesis, and it should be applied to the total synthesis of other molecules of this family which was underway in our laboratory.

4. Experimental

4.1. General

Dichloromethane (DCM) and tetrahydrofuran (THF) were distilled prior to use. All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous sodium sulfate before concentration in vacuo. All reported melting points were uncorrected. HPLC analysis of compound **12** was performed on Waters 600 system with a Chiralcel OD-H column (Dikma Chiralcel OD 10U 250 × 4.6 M, hexane/2-propanol = 95:5, flow rate = 1 mL/min, detected at 254 nm on a Prostar330 detector). TLC was monitored for all reactions. Purification of products was conducted by flash column chromatography on silica gel (200–300 mesh) purchased from Yan Tai Yuan Bo Silica Gel Co.

4.2. Compound 12

To a solution of **11** (274 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added imidazole (82 mg, 1.2 mmol) at 0 °C. After that, slow addition of TBSCl (166 mg, 1.1 mmol) in CH_2Cl_2 (15 mL) to the above solution. The reaction was stirred for 30 min and quenched with water and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (30:1, petrol/EtOAc) gave **12** as a colorless oil (369 mg, 95%). $[\alpha]_D^{25} = +21.6$ (*c* 4.0, $CHCl_3$); IR (neat): 3457, 2930, 1613, 1505 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.05 (s, 6H), 0.91 (s, 9H), 2.97 (d, $J = 3.6$ Hz, 1H), 3.48 (dd, $J_1 = 8.1$ Hz, $J_2 = 9.9$ Hz, 1H), 3.79 (s, 3H), 3.83 (dd, $J_1 = 3.3$ Hz, $J_2 = 9.9$ Hz, 1H), 4.98–5.02 (m, 1H), 5.06 (s, 2H), 6.52 (d, $J = 2.4$ Hz, 1H), 6.58 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.1$ Hz, 1H), 7.33–7.45 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −5.4, 18.3, 25.9, 55.2, 67.5, 69.4, 70.1, 99.1, 104.9, 121.2, 127.5, 127.6, 128.0, 128.6, 136.8, 157.3, 159.3. HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{32}O_4SiNa$, 411.2070; found, 411.2079.

4.3. Compound 8

A solution of oxalyl chloride (0.26 mL, 3 mmol) in dry CH_2Cl_2 (15 mL) at −78 °C was charged with dry DMSO (0.43 mL, 6 mmol in 5 mL CH_2Cl_2) and alcohol **13** (636 mg, 2 mol in 5 mL CH_2Cl_2). The reaction mixture was stirred at −78 °C for 30 min before Et_3N (1.1 mL, 8 mmol) was slowly added. After being stirred at −78 °C for another 30 min, the reaction mixture was allowed to warm to room temperature. Being quenched with H_2O (20 mL), the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (30:1, petrol/EtOAc) provided **8** as a colorless oil (556 mg, 88%). $[\alpha]_D^{25} = +177$ (*c* 2.0, $CHCl_3$); IR (neat): 2826, 1734, 1611, 1587, 1202, 1022 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.40 (s, 3H), 3.80 (s, 3H), 4.73 (s, 2H), 5.06 (s, 2H), 5.29 (s, 1H), 6.57 (s, 1H), 6.60 (s, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.34–7.45 (m, 5H), 9.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 55.7, 70.0, 78.2, 94.6, 99.6, 105.4, 115.1, 127.4, 128.0, 128.5, 130.6, 136.4, 158.2, 160.7, 198.3. HRMS (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{20}O_5$, 316.1311; found, 316.0945.

4.4. Compound 7

To a stirred solution of aldehyde **8** (443 mg, 1.4 mmol) in dry toluene (25 mL) was added $Ph_3P{=}CH(Me)CO_2Et$ (760 mg, 2.1 mmol), and the mixture was then heated at 100 °C with stirring for 12 h. The solvent was removed in vacuo and the residue washed with brine and extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (10:1, petrol/EtOAc) afforded **7** (555 mg, 1.4 mmol) as a colorless oil. $[\alpha]_D^{25} = +2.7$ (*c* 10.1, $CHCl_3$); IR (neat): 3032, 1710, 1652, 1242, 1201 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, $J = 7.2$ Hz, 3H), 1.94 (s, 3H), 3.37 (s, 3H), 3.79 (s, 3H), 4.17 (q, $J = 7.2$ Hz, 2H), 4.62 (s, 2H), 5.05 (s, 2H), 5.80 (d, $J = 8.8$ Hz, 1H), 6.52 (d, $J = 2.4$ Hz, 1H), 6.58 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.0$ Hz, 1H), 6.80 (d, $J = 8.8$ Hz, 1H), 7.33–7.44 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.7, 14.1, 55.3, 55.4, 60.6, 67.8, 70.0, 93.7, 99.2, 105.3, 120.8, 127.5, 128.0, 128.6, 128.7, 136.7, 140.2, 157.8, 159.7, 168.0. HRMS (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{28}O_6$, 400.1886; found, 400.2312.

4.5. Compound 14

To a solution of **7** (100 mg, 0.25 mmol) in THF (12 mL) and H_2O (4 mL) were added OsO_4 (4.5 mg, 0.0125 mmol) and NMO (32 mg, 0.275 mmol), and the reaction was stirred at room temperature for 4 h before being quenched with saturated Na_2SO_3 solution. The mixture was extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the diol mixture. Careful flash chromatography (100:1, CH_2Cl_2/CH_3COCH_3) afforded the desired diol as a colorless oil (64 mg, 70%). $[\alpha]_D^{25} = +20$ (*c* 2.0, $CHCl_3$); IR (neat): 3502, 1733, 1252, 1157, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, $J = 7.2$ Hz, 3H), 1.54 (s, 3H), 2.62 (br, 1H), 3.35 (s, 3H), 3.78 (d, $J = 6.3$ Hz, 1H), 3.80 (s, 3H), 3.97 (br, 1H), 4.15 (q, $J = 7.2$ Hz, 2H), 4.50 (s, 2H), 5.04 (s, 2H), 5.23 (d, $J = 6.3$ Hz, 1H), 6.53 (d, $J = 2.1$ Hz, 1H), 6.60 (dd, $J_1 = 2.1$ Hz, $J_2 = 8.1$ Hz, 1H), 7.30–7.44 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 23.4, 55.6, 56.4, 61.8, 70.1, 76.6, 78.0, 94.6, 99.2, 105.7, 119.0, 127.5, 128.1, 128.6, 129.2, 136.8, 158.7, 159.9, 175.8. HRMS (m/z): $[M]^+$ calcd for $C_{23}H_{30}O_8$, 434.1941; found, 434.1985.

4.6. Compound 15

Upon the addition of *para*-toluenesulfonic acid monohydrate (10 mg, 0.1 mmol) to a stirred solution of diol **l4** (434 mg, 1.0 mmol) and 2,2-dimethoxypropane (0.2 mL, 2 mmol) in CH_2Cl_2 (30 mL), the reaction was heated at 50 °C for 8 h before being quenched with H_2O (20 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) after separated from the organic layer. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (20:1, petrol/EtOAc) afforded acetonide **15** as a colorless oil (393 mg, 83%). $[\alpha]_D^{25} = +34$ (*c* 2.1, $CHCl_3$); IR (neat): 2988, 1739, 1611, 1505, 1060, 1022 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.30 (t, $J = 7.2$ Hz, 3H), 1.36 (s, 3H),1.39 (s, 3H), 1.54 (s, 3H), 3.32 (s, 3H), 3.80 (s, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.40 (d, $J = 7.2$ Hz, 1H), 4.46 (d, $J = 7.2$ Hz, 1H), 4.78 (d, $J = 9.0$ Hz, 1H), 5.04 (s, 2H), 5.17 (d, $J = 9.0$ Hz, 1H), 6.54 (d, $J = 2.4$ Hz, 1H), 6.60 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.4$ Hz, 1H), 7.33–7.46 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 19.1, 25.7, 28.1, 55.7, 56.4, 61.3, 70.0, 82.0, 82.7, 94.2, 99.3, 105.6, 109.4, 119.6, 127.6, 128.0, 128.6, 129.7, 136.8, 159.2, 159.8, 173.0. HRMS (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{34}O_8$, 474.2254; found, 474.2046.

4.7. Compound 16

To a solution of **15** (237 mg, 0.5 mmol) in ethanol (8 mL) and methanol (2 mL) was added Raney-Ni (100 mg) in one portion. The reaction mixture was stirred under atmosphere of H_2 for 24 h before filtering through a pad of Celite. The pad was washed repeatedly with ethyl acetate and the wash was combined with filtrate. Concentration in vacuo provided compound **16** as a white solid (346 mg, 90%). Mp: 97–99 °C; $[\alpha]_D^{25} = +90$ (*c* 4.2, $CHCl_3$); IR (neat) 3409, 1615, 1510, 1272, 1200, 1023, 1075 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, $J = 7.2$ Hz, 3H), 1.37 (s, 3H), 1.39 (s, 3H), 1.54 (s, 3H), 3.31 (s, 3H), 3.72 (s, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.39 (d, $J = 7.8$ Hz, 1H), 4.46 (d, $J = 7.8$ Hz, 1H), 4.77 (d, $J = 8.7$ Hz, 1H), 5.13 (d, $J = 8.7$ Hz, 1H), 6.05 (br, 1H), 6.27 (s, 1H), 6.32 (d, $J = 8.1$ Hz, 1H), 7.20 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 19.1, 25.7, 28.0, 55.5, 56.4, 61.5, 82.1, 82.8, 94.1, 99.1, 107.6, 109.6, 118.3, 129.7, 157.1, 159.3, 173.0. HRMS (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{28}O_8$, 384.1784; found, 384.2086.

4.8. Compound 6

Dicyclohexylcarbodiimide (DCC) (272 mg, 1.0 mmol) was added to a solution of propiolic acid (93 mg, 1.0 mmol), dimethylaminopyridine (DMAP) (10 mg, 10% mmol), and phenol **16** (255 mg, 0.66 mmol) in 20 mL CH_2Cl_2 at 0 °C under argon. The reaction mixture was stirred at the same temperature overnight. After filtering off the precipitate, the filtrate was concentrated and purified by flash chromatography. Compound **6** was obtained as a white solid (305 mg, 70%). Mp: 134–136 °C; $[\alpha]_D^{25} = +55$ (*c* 1.6, $CHCl_3$); IR (neat) 2121, 1736, 1263, 1197, 1102, 1025 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, $J = 7.2$ Hz, 3H), 1.33 (s, 3H), 1.37 (s, 3H), 1.52 (s, 3H), 3.07 (s, 1H), 3.30 (s, 3H), 3.82 (s, 3H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.44 (s, 2H), 4.68 (d, $J = 6.3$ Hz, 1H), 5.21 (d, $J = 6.3$ Hz, 1H), 6.67 (d, $J = 1.5$ Hz, 1H), 6.79 (dd, $J_1 = 1.5$ Hz, $J_2 = 6.3$ Hz, 1H), 7.44 (d, $J = 6.3$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 19.3, 25.6, 28.0, 55.9, 56.5, 61.4, 69.6, 74.2, 76.6, 82.1, 82.7, 94.7, 104.5, 109.5, 113.2, 125.7, 129.3, 150.3, 150.7, 158.8, 172.9. HRMS (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{28}O_9$, 436.1733; found, 436.1784.

4.9. Compound 5

A solution of **6** (436 mg, 1.0 mmol) in 8 mL THF and 2 mL 6 M HCl was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue was washed with brine and extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine, dried over

anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (5:1, petrol/EtOAc) afforded lactone **5** as a colorless oil (358 mg, 70%). $[\alpha]_D^{25} = +17$ (c 1.0, $CHCl_3$); IR (neat): 2988, 1739, 1611, 1505, 1060, 1022 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3H), 1.64 (s, 1H), 2.74 (s, 1H), 3.11 (s, 1H), 3.85 (s, 3H), 4.36 (d, $J =$ 3.3 Hz, 1H), 6.03 (d, $J = 3.3$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.83 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.7$ Hz, 1H), 7.47 (d, $J =$ 8.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 55.8, 74.0, 75.0, 76.8, 77.2, 79.1, 104.3, 113.4, 120.0, 128.5, 150.8, 150.9, 156.6, 176.4. HRMS (m/z): $[M+NH_4]^+$ calcd for $C_{26}H_{38}O_8N$, 324.1078; found, 324.0154.

4.10. Compound 2

A portion of aryl alkynoate (22 mg, 71 μmol) was mixed with $AuCl_3$ (1 mg, 5 mol %) and AgOTf (3 mg, 15 mol %) in 1.5 mL of dichloromethane and stirred at 40 °C for 8 h until the starting material had disappeared. The residue was purified by flash chromatography (2:1, petrol/EtOAc) to give the natural product hydramicromelin B (10 mg, 50%). $[\alpha]_D^{25} = +5$ (c 0.2, C_5H_5N); IR 1711, 1540, 1653 cm^{-1}. ^1H NMR (300 MHz, C_5D_5N): δ 1.97 (s, 3H), 3.67 (s, 3.65), 5.15 (d, $J = 7.5$ Hz, 1H), 5.86 (d, $J =$ 7.5 Hz, 1H), 6.34 (d, $J = 9.3$ Hz, 1H), 6.88 (s, 1H), 7.69 (s, 1H). ^{13}C NMR (75 MHz, C_5D_5N): δ 19.1, 56.3, 76.5, 79.1, 80.6, 99.8, 112.6, 113.7, 123.4, 128.4, 143.7, 156.5, 160.6, 179.1. HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{15}O_7$, 307.0735; found, 307.0812.

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8. Crystal data for compound **6**: $C_{22}H_{28}O_9$, $M = 436.44$, $0.59 \times 0.42 \times 0.41$ mm^3, triclinic, space group $P\bar{1}$ (No. 1), $a = 10.1759(8)$, $b = 11.0415(12)$, $c = 11.2677(13)$ Å $\alpha =$ 95.662(2)°, $\beta = 96.243(2)°$, $\gamma = 113.477(3)°$, $V =$ 1140.2(2) $Å^3$, $Z = 2$, $D_c = 1.271$ g/cm_3, $F(000) = 464$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 298(2)$ K, $2\theta_{max} = 50.0°$, 5939 reflections collected, 3932 unique ($R_{int} = 0.0265$). Final GooF = 1.004, $R_1 = 0.0501$, $wR_2 = 0.1191$, R indices based on 2270 reflections with $I > 2\sigma(I)$ (refinement on F^2), 295 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.099$ mm^{-1}.
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