Supporting Information
for DOI: 10.1055/s-0034-1380172
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SUPPORTING INFORMATION (I)

Total Synthesis of Two Pyrrole Spiroketal Alkaloids-Pollenopyrroside A and Capparisine B

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Experimental Section

General

DMF was dried by distillation over CaH₂. Other chemicals were used as received, and all reactions conducted under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200–300 meshes) was used for column chromatography. Melting points were determined with a SGW X-6 melt instrument and uncorrected. Optical rotations were measured on a DIP-370 polarimeter at the sodium D line (λ = 589 nm) at 28°C. ¹H NMR, ¹³C NMR, ¹H-¹H COSY, HSQC and HMBC spectra were recorded on Bruker Avance 400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. HRMS data were determined on ESI-MS spectrometer. All microwave-assisted reactions were carried out in microwave synthesis / extraction apparatus (Beijing XiangHu Science and Technology Development Co., LTD).

1-(((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3-a-yl)methyl)-1H-pyrrole-2,5-dicarbaldehyde (8): Potassium carbonate (10g, 36.88mmol) was added to a solution of H₂O (80mL) and 50mL formalin. Then 5g compound 6 was added and stirred under m.w. at 80°C with 500W of microwave irradiation power for 200min. Then the reaction mixture extracted with ethyl acetate (100mL*3). The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude reaction mixture was solved in acetone, then MnO₂ (10g) was added. The mixture stirred for 10h, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (20% EtOAc/hexane) to furnish 8 (5.14 g, 87%) as faint yellow solid. ¹H NMR (400 MHz, CDCl₃) δ
9.89 (s, 2H), 6.98 (s, 2H), 5.25 (d, J = 14.5 Hz, 1H), 5.05 (d, J = 14.5 Hz, 1H), 4.54 (dd, J = 7.9, 2.6 Hz, 1H), 4.37 (d, J = 2.6 Hz, 1H), 4.17 (dd, J = 7.9, 2.0 Hz, 1H), 3.84 (dd, J = 13.1, 2.0 Hz, 1H), 3.72 (d, J = 13.1 Hz, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.19 (s, 3H). $^{13}$C NMR (100 MHz, CDCl3) δ 181.9, 137.1, 119.7, 109.0, 108.8, 101.6, 71.5, 70.2, 70.3, 61.4, 50.4, 26.3, 25.8, 24.6, 23.6. HRMS (ESI) calcd for C$_{18}$H$_{24}$NO$_{7}$ [M+H]$^+$ 366.1553, found 366.1547.

1-(((3aS,6R,7R,7aS)-6,7-dihydroxy-2,2-dimethyltetrahydro-3aH-[1,3]dioxolo[4,5-b]pyran-3a-yl)methyl)-1H-pyrrole-2,5-dicarbaldehyde (9): Compound 8 (1g) was added in the mixture of CH$_3$CN (90mL) and H$_2$O (10mL) at 0°C. DDQ (124mg, 0.55mmol) was added. The reaction mixture was stirred at 80°C for 5h. Then concentrated under reduced pressure. The crude product dissolved in EtOAc, washed by aqueous solution of sodium hydroxide (4%). The mixture filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (50% EtOAc/hexane) to furnish 9 (756 mg, 85%) as colorless oil. $^1$H NMR (400 MHz, CDCl3) δ 9.82 (s, 2H), 7.01 (s, 2H), 5.25 (H-1, d, J = 14.4 Hz, 1H), 5.20 (H-1, d, J = 14.4 Hz, 1H), 4.27 (H-4, dd, J = 5.5, 3.0 Hz, 1H), 4.16 (H-3, d, J = 3.0 Hz, 1H), 4.01 (H-5, dd, J = 4.5, 5.5 Hz, 1H), 3.84 (H-6, dd, J = 12.3, 4.5 Hz, 1H), 3.77 (H-6, dd, J = 12.3, 5.5 Hz, 1H), 1.43 (s, 3H), 1.22 (s, 3H). $^{13}$C NMR (100 MHz, CDCl3) δ 182.4, 137.2, 121.5, 110.5, 101.3, 77.0, 66.2, 63.7, 63.5, 49.1, 27.0, 25.0. HRMS (ESI) calcd for C$_{13}$H$_{10}$NO$_2$Na [M+Na]$^+$ 348.1059, found 348.1058.

1-(((3aS,6R,7R,7aS)-6,7-dihydroxy-2,2-dimethyltetrahydro-3aH-[1,3]dioxolo[4,5-b]pyran-3a-yl)methyl)-5-(5,5-dimethyl-1,3-dioxan-2-yl)-1H-pyrrole-2-carbaldehyde (10). NPG (307 mg, 2.95 mmol) and PTSA (28 mg, 0.15 mmol) were added to a solution of compound 9 (800 mg, 2.46 mmol) in 50 mL of CH$_2$Cl$_2$ and the mixture was stirred for 5 h. The reaction mixture was washed with 2M Na$_2$CO$_3$, extracted with EtOAc (2 × 200 mL) and the organic layer was dried over
$\text{Na}_2\text{SO}_4$. Evaporation of the solvent under reduced pressure followed by column chromatography (50% EtOAc/hexane) yielded 10 (982 mg, 97%) as a white solid. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 9.45 (s, 1H), 7.00 (d, $J = 4.2$ Hz, 1H), 6.57 (d, $J = 4.2$ Hz, 1H), 5.82 (s, 1H), 4.25 (d, $J = 2.7$ Hz, 1H), 4.23 – 4.17 (m, 1H), 4.00 (dd, $J = 12.3$, 4.0 Hz, 1H), 3.91 (dt, $J = 6.0$, 3.9 Hz, 1H), 3.67 (d, $J = 11.3$, 1H), 3.62 (d, $J = 11.3$ Hz, 1H), 1.55 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H). HRMS (ESI) calcd for C$_{20}$H$_{30}$NO$_8$ [M+H]$^+$ 412.1971, found 412.1969.

1-(((3aS,6R,7R,7aS)-6,7-bis(benzyloxy)-2,2-dimethyltetrahydro-3aH-[1,3]dioxolo[4,5-b]pyran-3a-yl)methyl)-5-(5,5-dimethyl-1,3-dioxan-2-yl)-1H-pyrrole-2-carbaldehyde(10a): To a stirred solution of the NPG protected compound 10 (900 mg, 2.2 mmol) in 30 mL of dry DMF and after cooling in an ice-salt bath, NaH (35%, 450 mg, 6.6 mmol) was added. After 20 min stirring, BnCl (0.6 mL, 5.3 mmol) was added dropwise. After 2h stirring, careful methanolysis (10 mL) was then effected. The mixture was diluted in water (100 mL) and extracted with EtOAc (3×150 mL). The combined organic fractions were washed with water (3×50 mL), satd NaCl (50 mL), then dried over Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure followed by column chromatography (20% EtOAc/hexane) yielded 10a (1.138 g, 88%) as a colorless oil. $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 9.49 (s, 1H), 7.42 – 7.27 (m, 10H), 6.85 (d, $J = 4.1$ Hz, 1H), 6.46 (d, $J = 4.1$ Hz, 1H), 5.71 (s, 1H), 4.87 (d, $J = 11.9$ Hz, 1H), 4.74 (d, $J = 11.9$ Hz, 1H), 4.63 – 4.53 (m, 4H), 4.23 (d, $J = 3.5$ Hz, 1H), 4.16 (t, $J = 2.8$ Hz, 1H), 4.04 (dd, $J = 10.7$, 9.3 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.80 (dd, $J = 10.9$, 3.9 Hz, 1H), 3.67 (ddd, $J = 20.7$, 11.0, 2.6 Hz, 2H), 3.52 (d, $J = 10.5$ Hz, 2H), 1.39 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H), 0.74 (s, 3H). $^{13}$C NMR (100 MHz, CDCl3) $\delta$ 180.0, 138.1, 133.8, 128.8, 1286, 128.5, 127.8, 127.8, 127.5, 111.0, 109.0, 102.5, 96.0, 78.1, 77.2, 73.6, 72.5, 72.4, 71.6, 60.9, 47.4, 463, 30.3, 27.9, 26.1, 22.9, 21.9. HRMS (ESI) calcd for C$_{34}$H$_{42}$NO$_8$ [M+H]$^+$ 592.2910, found
592.2914.

1-(((3S,4S,5R)-4,5-bis(benzyloxy)-2,3-dihydroxytetrahydro-2H-pyran-2-yl)methyl)-1H-pyrrole-2,5-dicarbaldehyde(11): Compound 10a (1g, 1.69 mmol) was stirred in an aqueous solution of CH\textsubscript{3}COOH (50\%) at 100°C for 15h. Then the solvent was removed under reduced pressure. The residue was purified by flash column chromatography over silica gel (50\% EtOAc/ hexane) to give 11 (728 mg, 92.5\%) as colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.83 (s, 2H), 7.48 – 7.27 (m, 10H), 7.00 (s, 2H), 5.09 (H-1', d, \(J = 14.6\) Hz, 1H), 4.89 (H-1', d, \(J = 14.6\) Hz, 1H), 4.72 – 4.63 (m, 1H), 4.60 (d, \(J = 12.0\) Hz, 1H), 4.57 – 4.46 (m, 1H), 4.21 (s, 1H), 4.16 – 4.05 (m, 1H), 4.03 (H-3,d, \(J = 9.6\) Hz, 1H), 3.87 (ddd, \(J = 22.3, 7.0, 2.2\) Hz, 1H), 3.81 – 3.72 (m, 1H), 3.70 (s, 1H), 3.64 (dd, \(J = 9.5, 3.1\) Hz, 1H). HRMS (ESI) calcd for C\textsubscript{26}H\textsubscript{28}NO\textsubscript{7} [M+H]\textsuperscript{+} 466.1866, found 466.1872.

1-(((3S,4S,5R)-4,5-bis(benzyloxy)-2,3-dihydroxytetrahydro-2H-pyran-2-yl)methyl)-5-(hydroxymethyl)-1H-pyrrole-2-carbaldehyde(12): To a solution of dialdehyde 11 (500 mg, 1.1 mmol) in dry methanol (40 mL) at 0°C was added sodium borohydride (10.2 mg, 0.27 mmol) and stirred at the same temperature for 15 min before it was quenched with water. The aqueous layer was extracted with CH\textsubscript{3}Cl\textsubscript{2} (2 × 200 mL) and the combined extracts were washed with brine, dried by Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel (40 \% EtOAc/ hexane) to give mono-aldehyde 12 (450 mg, 90\%) as colorless oil.

(2S,3S,4S,5R)-4,5-bis(benzyloxy)-3-hydroxy-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carbaldehyde(3) and (2R,3S,4S,5R)-4,5-bis(benzyloxy)-3-hydroxy-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carbaldehyde(4): To a stirred solution of hemiketal compound 12 (400 mg, 1.44 mmol) in CH\textsubscript{3}Cl\textsubscript{2} (20 mL) at 0 °C was added
p-toluenesulfonic acid (20 mg, 0.11 mmol) and stirred at ambient temperature for 8 h. After this, the reaction mixture was partitioned between aqueous saturated Na₂CO₃ solution and extracted with EtOAc (3 ×50 mL). The organic extracts were combined, washed with brine, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. Anomeric mixture was separated by using silica gel column chromatography (30% EtOAc/hexane) to give anomers 3 (84 mg, 22%) as colorless oil and 4 (256 mg, 67%) as colorless oil. 3: ¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 7.39 – 7.26 (m, 10H), 6.92 (d, J = 4.1 Hz, 1H), 6.01 (d, J = 4.1 Hz, 1H), 5.04 (d, J = 15.5 Hz, 1H), 4.90 (d, J = 15.5 Hz, 1H), 4.84 (d, J = 14.7 Hz, 1H), 4.71 – 4.64 (m, 3H), 4.61 (d, J = 12.2 Hz, 1H), 4.31 (d, J = 14.1 Hz, 2H), 4.20 (d, J = 7.8 Hz, 1H), 4.01 (dd, J = 12.3, 5.4 Hz, 1H), 3.85 (ddd, J = 5.4, 3.1, 2.7 Hz, 1H), 3.72 (dd, J = 7.8, 3.1 Hz, 1H), 3.54 (dd, J = 12.3, 2.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 137.9, 137.9, 135.1, 131.3, 128.9, 128.5, 128.45, 127.9, 127.8, 127.8, 124.4, 104.8, 96.9, 77.33, 76.7, 72.3, 71.6, 71.5, 71.3, 65.6, 61.6, 58.4, 29.7. HRMS (ESI) calcd for C_{26}H_{28}NO_{6} [M+H]^+ 450.1917, found 450.1908.

4: ¹H NMR (400 MHz, CDCl₃) δ 9.47 (s, 1H), 7.38 – 7.28 (m, 10H), 6.90 (d, J = 4.1 Hz, 1H), 5.99 (d, J = 4.1 Hz, 1H), 4.91 (d, J = 15.3 Hz, 1H), 4.79 (d, J = 15.3 Hz, 1H), 4.71 (d, J = 12.3 Hz, 1H), 4.66 (d, J = 11.8 Hz, 1H), 4.62 (s, 2H), 4.58 (d, J = 11.9 Hz, 1H), 4.14 (d, J = 10.1 Hz, 1H), 3.93 – 3.80 (m, 3H), 3.59 (d, J = 12.4 Hz, 1H). ¹³C NMR (100MHz, CDCl₃) δ 178.7, 137.9, 137.8, 133.6, 131.5, 130.9, 128.6, 128.46, 127.9, 127.8, 127.8, 104.7, 96.5, 77.34, 76.7, 72.4, 71.8, 71.4, 69.7, 61.4, 57.9, 48.8, 29.7. HRMS (ESI) calcd for C_{25}H_{28}NO_{6} [M+H]^+ 450.1917, found 450.1911.

O-[(2S,3S,4R,5R)-4,5-bis(benzyloxy)-6'-formyl-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazin]-3-yl] S-methyl carbonodithioate (13a): To a stirred mixture of 12a (200 mg, 0.11 mmol) and iminazole (5 mg) in dry THF at 0°C, NaH (73 mg, 1.07 mmol) was added. After 20 min,
CS₂ (81 μL, 1.33 mmol) and CH₃I (50 μL, 0.8 mmol) was added. The mixture was stirred for 30 min before water was added dropwise. The reaction mixture was extracted with EtOAc (3 × 50 mL). The organic extracts were combined, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. The residue was purified by flash column chromatography over silicagel (20% EtOAc/ hexane) to give xanthates 13a (221 mg, 92%) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 7.50 – 7.26 (m, 6H), 6.90 (d, J = 4.1 Hz, 1H), 6.10 (d, J = 3.2 Hz, 1H), 6.01 (d, J = 4.1 Hz, 1H), 4.89 (dd, J = 7.6, 4.1 Hz, 2H), 4.76 – 4.70 (m, 1H), 4.64 (d, J = 14.3 Hz, 1H), 4.50 (d, J = 11.9 Hz, 1H), 4.44 (d, J = 11.8 Hz, 1H), 4.10 (t, J = 10.4 Hz, 1H), 4.03 (t, J = 3.0 Hz, 1H), 3.96 (d, J = 14.3 Hz, 1H), 3.83 – 3.73 (m, 1H), 3.68 (dd, J = 10.4, 4.4 Hz, 1H), 2.59 (s, 2H).

HRMS (ESI) calcd for C₂₈H₃₀NO₂S₂ [M+H]+ 540.1515, found 540.1510.

(2R,4S,5R)-5-(benzyloxy)-4-hydroxy-1',3,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carbaldehyde (14a): A mixture of 13a (100 mg, 0.19 mmol) and Et₃SiH (148 μL, 0.93 mmol) in dioxane (5mL) was heated to 90°C, a solution of BPO (45mg, 0.19mmol) in dioxane (5mL) was added. Then the mixture was stirred at 100°C for 2h, cooled to ambiance temperature. NaOH aqueous (8%, 5mL) was added. The reaction mixture was extracted with EtOAc (3 × 20 mL).

The organic extracts were combined, dried over anhydrous Na₂SO₄, evaporated under reduced pressure. The residue was purified by flash column chromatography over silicagel (20% EtOAc/ hexane) to give 14a (46 mg, 72%) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 7.46 – 7.27 (m, 5H), 6.91 (d, J = 4.1 Hz, 1H), 6.01 (d, J = 4.0 Hz, 1H), 4.83 (d, J = 11.2 Hz, 1H), 4.57 (d, J = 14.0 Hz, 1H), 4.47 (d, J = 11.3 Hz, 1H), 4.02 (d, J = 14.0 Hz, 1H), 3.96 (d, J = 3.2 Hz, 1H), 3.81 (dd, J = 11.5, 6.8 Hz, 1H), 3.66 – 3.56 (m, 1H), 2.45 (dd, J = 15.0, 3.5 Hz, 1H), 1.78 (dd, J = 15.0, 3.5 Hz, 1H). δ C (101 MHz, CDCl₃) 178.86, 137.79, 134.85, 131.01, 128.55, 127.99, 127.97, 124.38, 104.89,
93.26, 72.74, 70.69, 65.88, 60.98, 57.60, 51.80, 33.86. HRMS (ESI) caled for C_{19}H_{22}NO_{5} [M+H]^+ 344.1498, found 344.1494.

(2R,4S,5R)-4,5-dihydroxy-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carb aldehyde(15a): TiCl₄ (25μL, 0.15mmol) was added in 14a (50mg, 0.15mmol) and CH₂Cl₂ at -10°C. The mixture was stirred for 2h at -10°C before aqueous saturated Na₂CO₃ was added. Then the mixture was filtered over kieselguhr, extracted with EtOAc (3 x 20 mL), dried over anhydrous Na₂SO₄, evaporated under reduced pressure. The residue was purified using silica gel column chromatography to yield 1 (32 mg, 87%). [α]_{D}^{23} = +121.5 (c 0.08, MeOH). m.p. = 159-161°C.

¹H NMR (400 MHz, CDCl₃) δ 9.46 (s, 1H), 6.92 (d, J = 4.1 Hz, 1H), 6.03 (d, J = 4.0 Hz, 1H), 4.88 (s, 2H), 4.58 (d, J = 14.2 Hz, 1H), 4.07 (d, J = 14.2 Hz, 1H), 3.76 (d, J = 8.2 Hz, 1H), 3.59 (s, 1H), 2.30 (dd, J = 14.8, 3.1 Hz, 1H), 2.00 (dd, J = 14.8, 3.4 Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ178.9, 131.2, 123.9, 105.0, 94.6, 77.2, 67.0, 65.7, 60.2, 57.89, 51.6, 37.5. HRMS (ESI) caled for C₁₂H₁₇NO₅ [M+H]^+ 254.1028, found 254.1024.

O-((2R,3S,4R,5R)-4,5-bis(benzyloxy)-6'-formyl-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazin]-3-yl) S-methyl carbonodithioate (13b): Compound 13b (95%) was prepared from 12b following the same method outlined above for the preparation of same compounds from 13a. ¹H NMR (400 MHz, CDCl₃) δ 9.46 (s, 1H), 7.42 (ddd, J = 30.1, 15.9, 5.2 Hz, 6H), 6.88 (d, J = 4.0 Hz, 1H), 6.61 (d, J = 9.9 Hz, 1H), 5.99 (d, J = 3.9 Hz, 1H), 4.92 (d, J = 15.3 Hz, 1H), 4.77 (d, J = 12.8 Hz, 1H), 4.71 (d, J = 15.9 Hz, 1H), 4.63 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 12.2 Hz, 1H), 4.31 (t, J = 6.7 Hz, 1H), 4.22 (d, J = 14.3 Hz, 1H), 4.12 (d, J = 10.0 Hz, 1H), 3.85 (d, J = 10.0 Hz, 1H), 3.64 (s, 1H), 2.59 (s, 2H). HRMS (ESI) caled for C_{28}H_{38}NO_{5}S₂ [M+H]^+ 540.1515, found 540.1509.

(2S,4S,5R)-5-(benzylxy)-4-hydroxy-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazin
e]-6'-carbaldehyde (14b): Compound 14b (78%) was prepared from 13b following the same method outlined above for the preparation of same compounds from 14a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.45 (s, 1H), 7.42 – 7.28 (m, 5H), 6.90 (d, $J = 4.1$ Hz, 1H), 5.99 (d, $J = 4.1$ Hz, 1H), 4.78 (d, $J = 15.4$ Hz, 1H), 4.75 – 4.67 (m, 2H), 4.64 (s, 2H), 4.04 – 3.97 (m, 3H), 3.93 (dd, $J = 12.5$, 1.6 Hz, 1H), 3.75 – 3.61 (m, 2H), 2.04 (dd, $J = 11.5$, 3.9 Hz, 2H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 178.72, 170.64, 137.71, 134.11, 133.64, 131.17, 130.33, 129.33, 128.63, 128.47, 128.05, 127.70, 104.72, 95.46, 72.01, 70.38, 66.16, 64.99, 64.01, 57.66, 52.34, 32.88. HRMS (ESI) calcd for C$_{15}$H$_{21}$NO$_3$Na$^+$ [M+Na]$^+$ 366.1317, found 366.1312.

(2S,4S,5R)-4,5-dihydroxy-1',3,4,4',5,6-hexahydropyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carbaldehyde(2): Compound 2 (81%) was prepared from 14b following the same method outlined above for the preparation of same compounds from 1. $[\alpha]_{D}^{25} = +38.5$ (c 0.05, MeOH). m.p. = 166-169°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.46 (s, 1H), 6.92 (d, $J = 4.1$ Hz, 1H), 6.01 (d, $J = 4.1$ Hz, 1H), 4.82 (d, $J = 15.3$ Hz, 1H), 4.77 – 4.65 (m, 1H), 4.17 (ddd, $J = 11.4$, 5.4, 3.2 Hz, 1H), 4.02 (d, $J = 14.0$ Hz, 1H), 3.89 (dd, $J = 6.7$, 3.9 Hz, 2H), 3.88 (m, 1H), 3.81 (dd, $J = 12.9$, 1.6 Hz, 1H), 2.05 (dd, $J = 13.0$, 5.5 Hz, 1H), 1.91 (t, $J = 13.0$ Hz, 1H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 178.80, 134.05, 131.17, 123.97, 104.81, 95.42, 77.23, 67.39, 65.07, 64.53, 57.78, 52.22, 35.80. $^{13}$C NMR (100MHz, DMSO) $\delta$ 178.52, 134.58, 130.54, 104.75, 94.87, 66.64, 65.25, 63.98, 57.00, 51.69, 48.55, 34.90. HRMS (ESI) calcd for C$_{12}$H$_{16}$NO$_3$ [M+H]$^+$ 254.1028, found 254.1023.
Figure S1. Related NOESY of anomers 3 and 4.

Figure S2. Structure and key HMBC of 14a.

Figure S3. Key HMBC of 14b.
SUPPORTING INFORMATION (II)

Total Synthesis of Two Pyrrole Spiroketal Alkaloids-Pollenopyrroside A and Capparisine B

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