Supporting Information

Amide Alkaloids from *Scopolia tangerica*

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General experimental procedures

The analytical chromatography system consisted of a 2695 HPLC pump and a 2489 photodiode array detector system. The chromatographic system for purification consisted of a 2525 binary gradient pump and a 2489 ultraviolet-visible detection system. Data were collected and analyzed using Empower software version 3.0 and Masslynx software version 4.1. All instruments and workstations were purchased from Waters. Melting points were recorded on an X-4 melting point apparatus (Tai Guang) without correction. IR spectra were recorded with a Perkin-Elmer GS-II FTIR spectrometer (Perkin-Elmer), and UV spectra were acquired using an SP-1901 UV (Guang Pu). Optical rotations were obtained with a Perkin-Elmer 241 polarimeter. All NMR spectra were recorded on a Bruker FT-NMR Ultra Shield TM 600 MHz spectrometer with TMS (tetramethylsilane) as the internal standard. HRESIMS were obtained using an orbitrap LTQ-Orbitrap mass spectrometer (Thermo). Strong cation exchange (SCX) solid phase extraction (SPE) (20 g, 60 mL, 60 µm) cartridges, XCharge C18 (50 x 260 mm, 10 µm), XCharge C18 (20 x 250 mm, 10 µm), C8PN (10 x 150 mm, 5 µm), C8PN (20 x 250 mm, 10 µm) and XCharge SCX (20 x 250 mm, 10 µm) columns were purchased from Accorm Ltd. Co. Ca^{2+} responses were monitored by a fluorometric imaging plate reader assay (FLIPR).

The alkaloid-enriched fraction was separated by XCharge C18 column, and 15 fractions (Fr. 1 – Fr. 15) were obtained. Details are described in Fig. aS. Fr. 6 and Fr. 9 was purified by C8 PN. Compounds 9 (201.1 mg) and 10 (161.1 mg) were obtained from Fr. 6. Details are described in
**Fig. bS.** Compound 6 (198.4 mg) and 7 (49.6 mg) were obtained from Fr. 9. Details are described in **Fig. cS.** Fr. 11 and Fr. 14 were further separated by XCharge SCX. Details are described in **Figs. dS and eS.** Compounds 2 (50.1 mg), 3 (9.2 mg), 5 (571.5 mg), and 8 (553.2 mg) were obtained from Fr. 11. Six subfractions (Fr. 14A–Fr. 14G) from Fr. 14 were obtained. Fr. 14C and Fr. 14E were further purified by XCharge C18. Compound 11 (7.4 mg) was acquired from the subfraction Fr. 14C. Details are described in **Fig. fS.** Compounds 1 (8.3 mg) and 4 (313.3 mg) were acquired from the subfraction Fr. 14E. Details are described in **Fig. gS.** All compounds were desalted by C18 SPE and eluted with FA/methanol (5/1000, v/v). Compounds 1-11 are all formates.
The chromatogram for the alkaloid enriched fraction was obtained on XCharge C18 (50 x 250 mm, 10 μm). The mobile phases were A: ACN, B: 200 mM Na₂SO₄ (pH was adjusted to 2.3 by H₃PO₄ and ethanolamine), C: H₂O. Mobile phase concentrations were started at 5% A, 10% B and shifted to 15% A, 10% B over 30 min. The flow rate was 80.0 mL/min, and peaks were recorded at 210 nm.
Fig. bS Chromatogram for Fr. 6 was obtained on C8PN (10 × 150 mm, 5 μm). The mobile phases were A: ACN, B: 100 mM NaClO₄, C: 100 mM NaH₂PO₄ (pH was adjusted to 2.8 by 85% H₃PO₄), D: H₂O. Mobile phase concentrations were started at 5% A, 10% B, 5% C and shifted to 15% A, 10% B, 5% C, over 30 min. The flow rate was 3.0 mL/min, and peaks were recorded at 210 nm.

Fig. cS Chromatogram for Fr. 9 was obtained on C8PN (10 × 150 mm, 5 μm). The mobile phases were A: ACN, B: 100 mM NaClO₄, C: 100 mM NaH₂PO₄ (pH was adjusted to 2.8 by 85% H₃PO₄), D: H₂O. Mobile phase concentrations were started at 5% A, 10% B, 5% C and shifted to 15% A, 10% B, 5% C, over 30 min. The flow rate was 3.0 mL/min, and peaks were recorded at 210 nm.
Fig. dS Chromatogram for Fr. 11 was obtained on XCharge SCX (20 x 250 mm, 10 μm). The mobile phases were A: ACN, B: 100 mM NaH₂PO₄ (pH was adjusted to 2.8 by 85% H₃PO₄), C: H₂O. Mobile phase concentrations were started at 30% A, 30% B and shifted to 50% A, 30% B over 30 min. The flow rate was 20.0 mL/min, and peaks were recorded at 210 nm.
Chromatogram for Fr. 11 was obtained on XCharge SCX (20 x 250 mm, 10 μm). The mobile phases were A: ACN, B: 100 mM NaH₂PO₄ (pH was adjusted to 2.8 by 85% H₃PO₄), C: H₂O. Mobile phase concentrations were started at 30% A, 30% B and shifted to 50% A, 30%B over 30 min. The flow rate was 20.0 mL/min, and peaks were recorded at 210 nm.
Chromatogram for Fr. 14C was obtained on XCharge C18 (20 x 250 mm, 10 μm). The mobile phases were A: ACN, B: 0.1% FA. Mobile phase concentration was 7% A. The flow rate was 20.0 mL/min, and peaks were recorded at 210 nm.
**Fig. gS** Chromatogram for Fr. 14E was obtained on XCharge C18 (20 x 250 mm, 10 μm). The mobile phases were A: ACN, B: 0.1% FA. Mobile phase concentration was 7% A. The flow rate was 20.0 mL/min, and peaks were recorded at 210 nm.
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Carbon signal of formic acid
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Fig. 13S HMBC spectrum of 2 in DMSO-$_d_6$. 

HMBC correlations of formic acid
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(proton signal of formic acid)
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