Supporting Information

Identification and Characterization of Anticancer Compounds
Targeting Apoptosis and Autophagy from Chinese Native *Garcinia*

Species
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Isolation and identification of isobractatin and neobractatin

General experimental procedures
NMR spectra were recorded on a Bruker AV-400 spectrometer with TMS as the internal standard. A Waters 2535 Series machine equipped with a Xbridge C18 column (4.6 × 250 mm, 5 μm) was used for HPLC analysis. Column chromatography was performed with silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd.), Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Sweden), and reversed-phase C18 silica gel (50 μm, YMC, Kyoto, Japan). Analytical and preparative TLC were performed on precoated GF254 plates (0.25- or 0.5-mm thickness, Qingdao Haiyang Chemical Co. Ltd.). Detection was performed by spraying the plates with 10% sulfuric acid followed by heating.

Plant material
The trunks of *G. bracteata* were collected from Napo, Guangxi Province, People’s Republic of China, in October 2012, and authenticated by Professor Zhao Yiming, Guangxi Medicinal Garden. A voucher specimen was deposited in Guangxi Medicinal Garden (G. B. 00001) and the Innovative Research Laboratory of TCM, Shanghai University of Traditional Chinese Medicine (Herbarium No. GAR-004).

Isolation and purification procedures
The air-dried and powdered trunks of *G. bracteata* (4 kg) were extracted with 95% (v/v) ethanol (3 × 8L) and filtered at room temperature. Then the combined ethanol extract was evaporated by rotary evaporator to obtain a crude extract (754.8g) which was suspended in H₂O (2L) and then extracted with petroleum ether (PE), ethyl acetate and n-butyl alcohol (each, 3 ×2L), respectively. The combined EtOAc extracts (262.2 g) were evaporated to give a deep-brown gum and subjected to column chromatography (Φ10×75cm) on silica gel (3.0 kg, 200-300 mesh) eluted with a petroleum ether-acetone (v/v from 10:1 to 1:1) gradient system to furnish ten
fractions (Fr.A, 32.3g; Fr.B, 24.8g; Fr.C, 15.2g; Fr.D, 14.5g; Fr.E, 34.7g; Fr.F, 27.2g; Fr.G, 16.4g; Fr.H, 40.1g; Fr.I, 28.8g; Fr.J, 30.2g). The yellow powder of compound 1 (210mg) was obtained from Fraction B through repeated crystallization with acetone. The yellow precipitate from Fraction D (14.5g) was subjected to Sephadex LH-20 (3.4 × 160 cm) column chromatography by elution with methanol to afford three fractions (Fr.A1, 5.2g; Fr.A2, 4.6g; Fr.A3, 4.5g) on the basis of TLC analysis. Fraction A3 (4.5g) was subjected to column chromatography on silica gel (100g, 200-300 mesh) and eluted with chloroform to furnish nine subfractions (Fr.A3-1, 430mg; Fr.A3-2, 560mg; Fr.A3-3, 270mg; Fr.A3-4, 450mg; Fr.A3-5, 730mg; Fr.A3-6, 630mg; Fr.A3-7, 150mg; Fr.A3-8, 335mg; Fr.A3-9, 680mg) on the basis of TLC analysis. Fraction A3-7 was further performed on reversed-phase column eluted with methanol-water (from 75%- 90%) to obtain compound 2 (124mg). The purity of these two compounds was greater than 98%.

Identification of isolates

$^1$H and $^{13}$C NMR data of compound 1 and compound 2 identified them as isobractatin [1] and neobractatin [2], respectively, by comparison with published values.

**Compound 1 (isobractatin):** $^{13}$C NMR (101 MHz, DMSO) $\delta$ 203.81(C-6), 179.05(C-9), 167.69(C-3), 165.32(C-1), 155.80(C-4a), 135.59(C-8a), 133.94(C-18), 132.46(C-8), 117.79(C-17), 113.22(C-4), 100.66(C-9a), 91.68(C-2), 90.64(C-12), 90.61(C-10a), 83.78(C-5), 82.71(C-23), 48.40(C-22), 46.75(C-7), 42.62(C-11), 30.23(C-25), 28.77(C-24), 28.57(C-16), 25.37(C-19), 25.26(C-21), 23.29(C-14), 20.75(C-15), 16.52(C-20), 13.29(C-13). $^1$H NMR (400 MHz, DMSO) $\delta$ 13.20 (s, 1H), 7.52 (d, J = 7.0 Hz, 1H), 6.04 (d, J = 3.0 Hz, 1H), 4.42 (q, J = 6.5 Hz, 1H), 3.51 (dd, J = 6.9, 4.4 Hz, 1H), 2.67 (d, J = 9.2 Hz, 1H), 1.65 (s, 3H), 1.56 (s, 3H), 1.36 (d, J = 6.6 Hz, 3H), 1.29 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H), 1.01 (s, 3H).
Compound 2 (neobractatin): $^{13}$C NMR (101 MHz, DMSO) $\delta$ 200.29 (C-5), 178.29 (C-9), 167.40 (C-3), 162.53 (C-1), 159.48 (C-4a), 151.46 (C-12), 135.85(C-8), 135.76 (C-8), 133.61 (C-8a), 118.07 (C-22), 113.05 (C-4), 106.61 (C-13), 100.92 (C-9a), 97.57 (C-2), 83.96 (C-10), 79.30 (C-6), 44.95 (C-7), 41.85 (C-17), 40.98 (C-11), 32.46 (C-16), 30.48 (C-21), 29.61 (C-20, 14), 28.75 (C-15), 26.89 (C-25), 26.11 (C-19), 18.30 (C-24); $^1$H NMR (400 MHz, DMSO) $\delta$ 12.69 (s, 1H), 7.18 (d, $J = 6.8$ Hz, 1H), 6.33 (dd, $J = 17.4$, 10.6 Hz, 1H), 5.99 (s, 1H), 4.92 (t, $J = 7.2$ Hz, 1H), 4.84 (d, $J = 17.4$ Hz, 1H), 4.72 (d, $J = 10.6$ Hz, 1H), 3.83-3.76 (m, 1H), 3.34 (s, 1H), 2.51 (s, 2H), 2.32 (m, 1H), 2.28 (m, 1H), 2.23 (dd, $J = 9.6$, 4.1 Hz, 1H), 2.12-2.00 (m, 1H), 1.93-1.83 (m, 1H), 1.66 (s, 3H), 1.55 (s, 6H), 1.54 (s, 3H), 1.27 (s, 3H), 1.24 (s, 3H).
**Fig. 1S** $^{13}$C NMR spectrum of isobractatin.

**Fig. 2S** $^1$H NMR spectrum of isobractatin.
Fig. 3S $^{13}$C NMR and DEPT135 spectrum of neobractatin.
Fig. 4S $^1$H NMR spectrum of neobractatin.

Fig. 5S HSQC spectrum of neobractatin.
Fig. 6S HSBC spectrum of neobractatin.

References
