

## Supplementary Materials

# Stachydrine, a bioactive equilibrin for synephrine, identified from four *Citrus* Chinese herbs

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**Figure S1.** Color development reactions of choline (1), synephrine (2) and  $\gamma$ -aminobutyric acid (3) on thin layer plates.

**Figure S2.** The linearity correlations between the amounts ( $x$ ) and peak areas ( $y$ ), of stachydrine (a), choline (b) and synephrine (c).

**Figure S3.** Detection of choline analogs in samples originated from *Citrus* genus plants on thin layer plates.

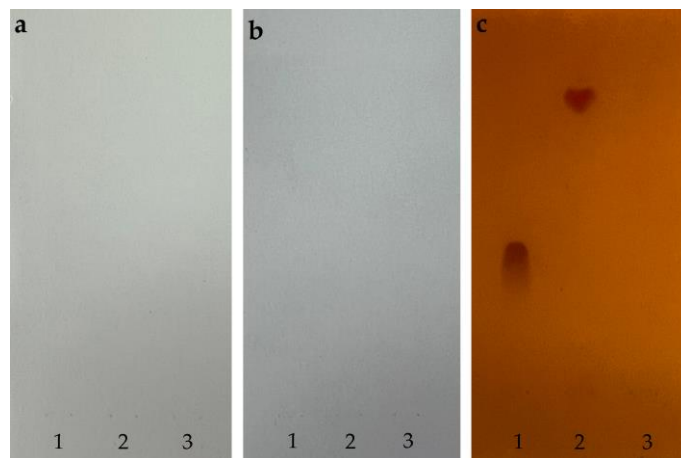
**Figure S4.** Detection of choline analogs in samples originated from other plants on thin layer plates.

**Figure S5.** <sup>1</sup>H (up), <sup>13</sup>C (middle) NMR and MS (down) spectra of compound 2.

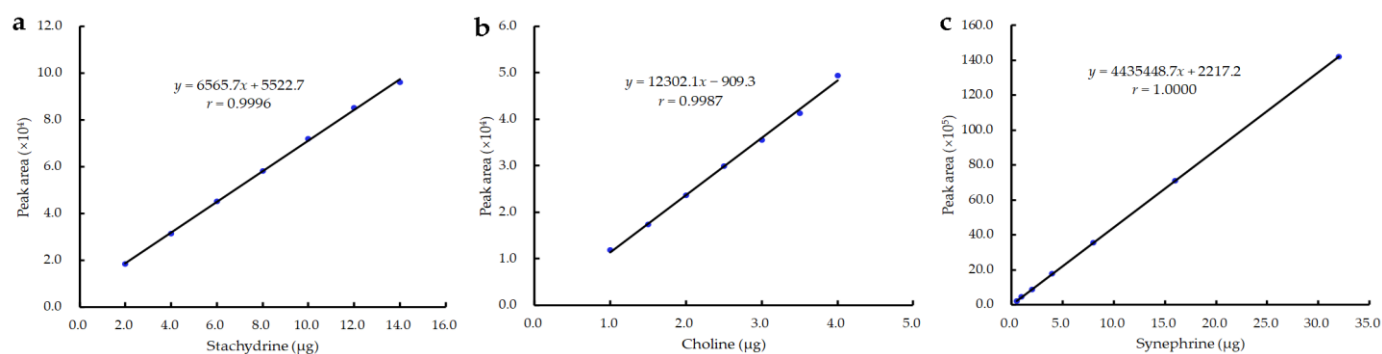
**Table S1.** The recovery of stachydrine ( $n = 9$ ).

**Table S2.** The recovery of choline ( $n = 9$ ).

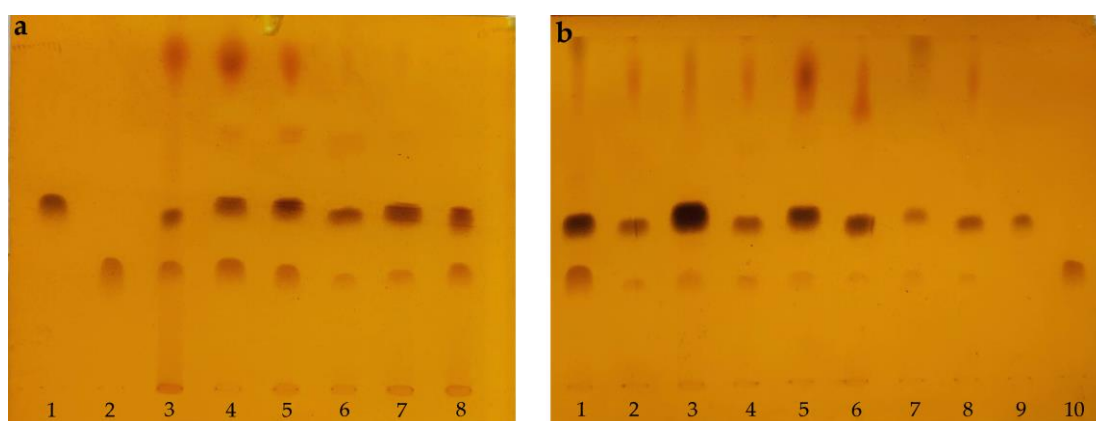
**Table S3.** The recovery of synephrine ( $n = 9$ ).



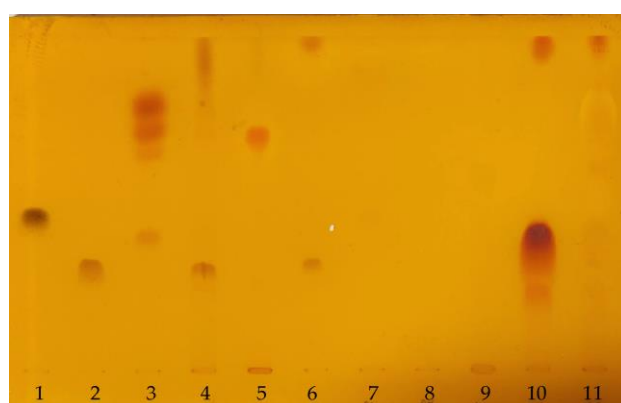
**Figure S1.** Color development reaction of choline (1), synephrine (2) and  $\gamma$ -aminobutyric acid (3) on thin layer plate. **a:** Dragendorff's reagent; **b:** Wagner reagent; **c:** improved Dragendorff's reagent.



**Figure S2.** The linearity correlations between the amounts ( $x$ ) and peak areas ( $y$ ), of stachydrine (**a**), choline (**b**) and synephrine (**c**).



**Figure S3.** Detection of choline analogs in samples originated from *Citrus* genus plants on thin layer plates. a: 1, stachydrine; 2, choline; and samples from herbs 3, *Chenpi*; 4, *Qingpi*; 5, *Zhishi*; 6, *Zhiqiao*; 7, *Xiangyuan*; and 8, *Foshou*, respectively. b: samples from the leaves (1) and fruits (2) of *Citrus aurantium* L.; from the leaves (3) and fruits (4) of *Citrus junos* Siebold ex Tanaka; from the leaves (5) and fruits (6) of *Citrus reticulata* Blanco 'Zhangtoughong'; from the leaves (7) and fruits (8) of the cultivated variety of *Citrus aurantium* L 'Chouchen'; (9) stachydrine and (10) choline.



**Figure S4.** Detection of choline analogs in samples originated from other plants on thin layer plates. 1, stachydrine; 2, choline; and herbs 3, *Huanglian*; 4, *Juhua*; 5, *Mahuan*; 6, *Chuanxiong*; 7, *Dafupi*; 8, *Banxia*; 9, *Duzhong*; 10, *Kushen*; and 11, *Gancao*.

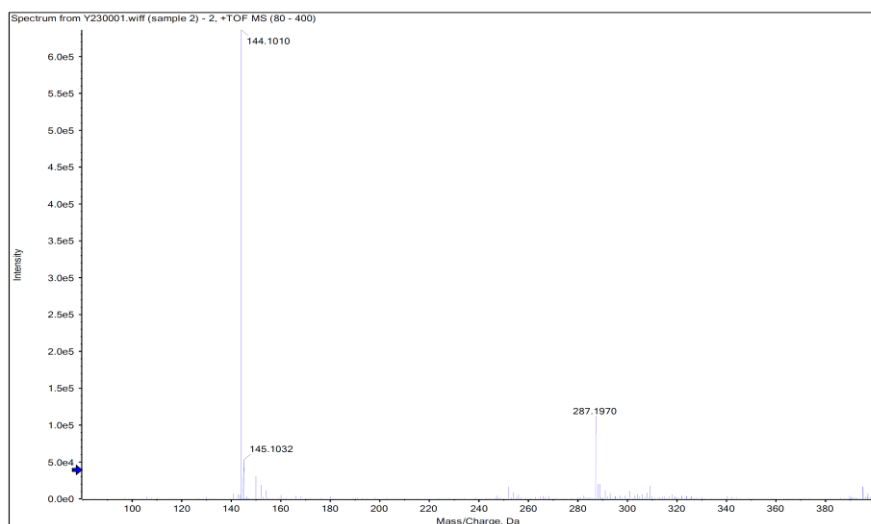
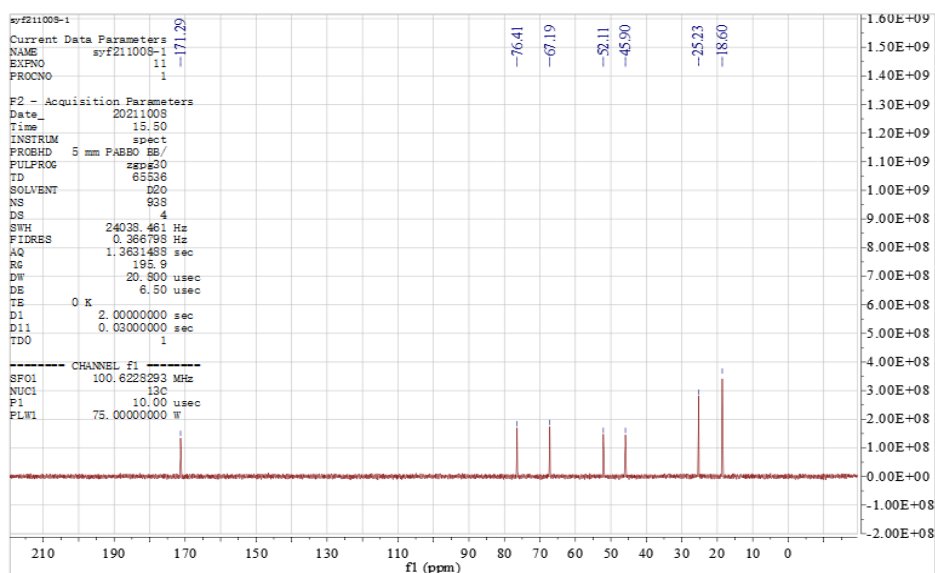
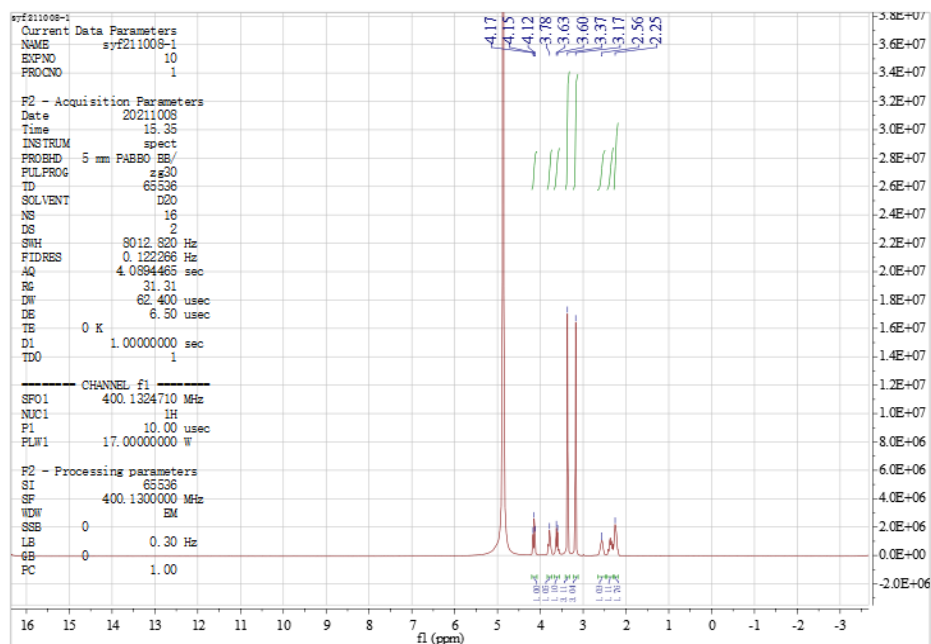


Figure S5.  $^1\text{H}$  (up),  $^{13}\text{C}$  (middle) NMR and MS (down) spectra of compound 2.

Table S1. The recovery of stachydrine ( $n = 9$ ).

| Sample power<br>(g) | Stachydrine in sample<br>(mg) | Stachydrine added<br>(mg) | Stachydrine tested<br>(mg) | Recovery<br>(%) | Average recovery<br>(%) | RSD<br>(%) |
|---------------------|-------------------------------|---------------------------|----------------------------|-----------------|-------------------------|------------|
| 0.5003              | 1.54                          | 6.50                      | 8.06                       | 101.30          | 100.28                  | 3.08       |
| 0.5004              | 1.50                          | 6.50                      | 7.96                       | 97.33           |                         |            |
| 0.5001              | 1.48                          | 6.50                      | 8.03                       | 103.38          |                         |            |
| 1.0001              | 2.90                          | 5.00                      | 7.95                       | 101.72          |                         |            |
| 1.0003              | 3.10                          | 5.00                      | 8.09                       | 99.68           |                         |            |
| 1.0003              | 3.03                          | 5.00                      | 8.14                       | 103.63          |                         |            |
| 1.4999              | 4.57                          | 3.50                      | 7.86                       | 95.40           |                         |            |
| 1.5003              | 4.40                          | 3.50                      | 8.04                       | 103.18          |                         |            |
| 1.5001              | 4.56                          | 3.50                      | 7.92                       | 96.93           |                         |            |

Table S2. The recovery of choline ( $n = 9$ ).

| Sample power<br>(g) | Choline in sample<br>(mg) | Choline added<br>(mg) | Choline tested<br>(mg) | Recovery<br>(%) | Average recovery<br>(%) | RSD<br>(%) |
|---------------------|---------------------------|-----------------------|------------------------|-----------------|-------------------------|------------|
| 0.5002              | 0.41                      | 2.60                  | 3.02                   | 102.44          | 101.04                  | 2.31       |
| 0.5003              | 0.42                      | 2.60                  | 3.01                   | 97.62           |                         |            |
| 0.5001              | 0.44                      | 2.60                  | 3.03                   | 97.73           |                         |            |
| 1.0004              | 0.84                      | 2.20                  | 3.05                   | 101.19          |                         |            |
| 1.0005              | 0.86                      | 2.20                  | 3.09                   | 103.49          |                         |            |
| 1.0001              | 0.85                      | 2.20                  | 3.07                   | 102.35          |                         |            |
| 1.5002              | 1.31                      | 1.70                  | 3.06                   | 103.82          |                         |            |
| 1.5000              | 1.29                      | 1.70                  | 3.01                   | 101.55          |                         |            |
| 1.4998              | 1.27                      | 1.70                  | 2.96                   | 99.21           |                         |            |

Table S3. The recovery of synephrine ( $n = 9$ ).

| Sample power<br>(g) | Synephrine in sample<br>(mg) | Synephrine added<br>(mg) | Synephrine tested<br>(mg) | Recovery<br>(%) | Average recovery<br>(%) | RSD<br>(%) |
|---------------------|------------------------------|--------------------------|---------------------------|-----------------|-------------------------|------------|
| 0.1000              | 1.10                         | 0.80                     | 1.95                      | 104.54          | 99.89                   | 3.19       |
| 0.1003              | 1.11                         | 0.80                     | 1.94                      | 102.70          |                         |            |
| 0.1001              | 1.08                         | 0.80                     | 1.90                      | 101.85          |                         |            |
| 0.1001              | 1.12                         | 1.00                     | 2.07                      | 95.53           |                         |            |
| 0.1000              | 1.08                         | 1.00                     | 2.05                      | 97.22           |                         |            |
| 0.1003              | 1.08                         | 1.00                     | 2.07                      | 99.07           |                         |            |
| 0.1002              | 1.10                         | 1.20                     | 2.26                      | 96.36           |                         |            |
| 0.1001              | 1.06                         | 1.20                     | 2.25                      | 99.05           |                         |            |
| 0.1005              | 1.11                         | 1.20                     | 2.34                      | 102.70          |                         |            |