

1 Supporting Information

2 for

3 **“Magnetic Solid Phase Extraction Coupled with *in-situ* Derivatization**
4 **for Highly Sensitive Analysis of Acidic Phytohormones in Rice Leaves**
5 **by UPLC-MS/MS”**

6
7 Jiu-Feng Liu, Jun Ding, Bi-Feng Yuan, Yu-Qi Feng*

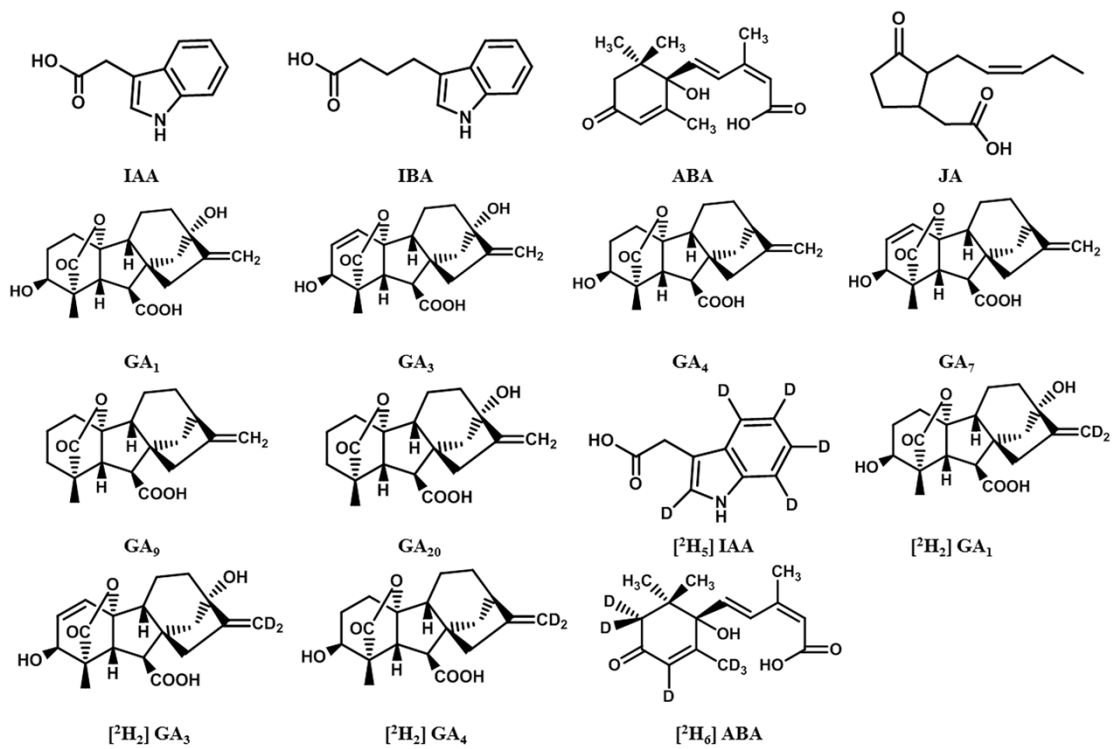
8
9 Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education),

10 Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China.

11 *Corresponding author: Yu-Qi Feng, Department of Chemistry, Wuhan University, Wuhan
12 430072, P.R. China. Tel: +86-27-68755595; Fax: +86-27-68755595; E-mail:
13 yqfeng@whu.edu.cn

14

15



17

18 **Figure S1.** Chemical structures of ten acidic phytohormones and five internal standards.

20 **Table S1.** MRM parameters of 15 acidic phytohormones and IS in UPLC-ESI-MS/MS.

Analytes	Scan mode	Precursor ion (m/z)	Product ion (m/z) ^a	Q1 pre bias (V)	CE (V)	Q3 pre bias (V)
GA ₁	-	347.3	229.1 /273.2	16/13	37/35	23/15
GA ₃	-	345.3	143.1 /--	16/--	29/--	25/--
GA ₄	-	331.2	213.1 /257.2	30/14	32/22	20/25
GA ₇	-	329.3	223.2 /--	21/--	17/--	22/--
GA ₉	-	315.3	253.2 /271.0	22/24	27/20	25/27
GA ₂₀	-	331.2	287.3 /225.2	29/16	21/26	18/21
ABA	-	263.2	153.1 /--	15/--	10/--	29/--
IAA	+	176.1	130.1 /103.2	-20/-20	-15/-33	-24/-19
JA	-	209.2	59.3 /--	17/--	16/--	19/--
IBA	-	202.1	62.25 /--	14/--	11/--	23/--
[² H ₂] GA ₁	-	349.3	231.2 /275.1	16/16	29/25	14/26
[² H ₂] GA ₃	-	347.3	143.2 /--	16/--	27/--	26/--
[² H ₂] GA ₄	-	333.3	215.2 /259.3	15/15	31/22	21/16
[² H ₆] ABA	-	269.2	159.1 /--	15/--	10/--	29/--
[² H ₅] IAA	-	179.0	159.8 /--	18/--	25/--	24/--

21 ^a The product ions in bold were used for quantification.

23 **Synthesis of BTA**

24 BTA was synthesized according to a previously reported method.¹ Briefly, bromine (41.2
25 mL) was added dropwise to a solution containing acetone (25 mL) and methanol (300 mL)
26 while stirring continuously in a water bath (25 °C). After all of the bromine was added, the
27 reaction mixture was stirred for another 2 h and then transferred to a fridge and kept at -18 °C
28 overnight. The crystal precipitate was collected via vacuum filtration. Next, the precipitate (12
29 g) was added into water (500 mL), and then 95% concentrated sulfuric acid (5 mL) was
30 slowly added. The reaction mixture was stirred for 48 h at 60 °C in a water bath. When the
31 solution was cooled down to the room temperature, dichloromethane (3 × 200 mL) was used
32 to extract. The organic extracts were combined, washed with saturated brine and dried over
33 anhydrous magnesium sulfate (MgSO₄). Subsequently, the organic solvent was removed by
34 evaporation under reduced pressure in a bath kept below 35 °C, and a light yellow liquid
35 consisting of 1,3-dibromoacetone was left. Finally, TMA (0.23 mL, 0.001 mol) was dissolved
36 in 4 mL toluene, and then was added dropwise during 3 h to the solution of 1,3-
37 dibromoacetone (2.16 g, 0.01 mol) in toluene (2 mL) stirring constantly at 0 °C. The
38 precipitate was collected via vacuum filtration and dissolved in absolute ethanol (1 mL) and
39 then re-precipitated with isopropyl ether (5 mL). The light yellow product was filtered off and
40 dried in vacuum desiccator over P₂O₅.

41 **Preparation of TiO₂/MHMSS**

42 TiO₂/magnetic hollow mesoporous silica sphere (MHMSS) was prepared according to
43 our previous work with slight modification.² Firstly, the hollow mesoporous silica spheres
44 (HMSS) were synthesized. Briefly, CTAB (19.6 g) was dissolved in water (337 mL). Then,

45 with the addition of solid $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (23.2 g), a clear solution was formed under stirring
46 at 30 °C till the $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was dissolved. Subsequently, ethyl acetate (35 mL) was added.
47 The mixture was stirred vigorously for 30 seconds followed by standing at 30 °C for 5 hours.
48 Then, the mixture was aged at 90 °C for 48 hours. Finally, the product was filtered and
49 washed with ethanol for several times. The filtered HMSS was dried in a vacuum oven and
50 calcined at 550 °C for 5 hours. Then magnetic nanoparticles were introduced into the hollow
51 core of HMSS via a vacuum impregnation of $\text{Fe}(\text{NO}_3)_3$. HMSS (2.4 g) was dispersed in
52 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution (24 g/L, 200 mL). The suspension was heated by
53 microwave oven till boiling. Then the Fe^{3+} entered into the hollow core of HMSS when the
54 suspension was cooled in ice water mixture. The process was repeated for several times until
55 water totally dried up. Afterward, the product was rinsed with ethanol (10 mL) twice and
56 dried again. The product was impregnated in ethylene glycol (1 mL) up to incipient wetness.
57 The impregnated sample was then heated under nitrogen at 450 °C for 2 hours. Finally, TiO_2
58 was loaded onto the obtained MHMSS by liquid phase deposition method. MHMSS (2.0 g)
59 was added into a solution (200 mL) of 0.1 M $(\text{NH}_4)_2\text{TiF}_6$ and 0.3 M H_3BO_3 in a PTFE
60 container. The mixture was heated at 35 °C for 12 h under continuous shaking after kept
61 under vacuum condition for 1 h. The resulting composite was washed with water thoroughly
62 and dried in a vacuum oven at 60 °C for 6 h. At last, the harvested products were subjected to
63 heat treatment under nitrogen up to a treatment of 300 °C at the rate of 1 K/min and kept at
64 this temperature for 2 h. The final products were collected for further use.

65

66 **References**

- 67 1. Y. Q. Huang, G. D. Ruan, J. Q. Liu, Q. Gao, Y. Q. Feng, *Anal. Biochem.*, 2011, **416**, 159-
68 166.
- 69 2. J. H. Wu, X. S. Li, Y. Zhao, Q. Gao, L. Guo, Y. Q. Feng, *Chem. Commun.*, 2010, **46**,
70 9031.
- 71
- 72