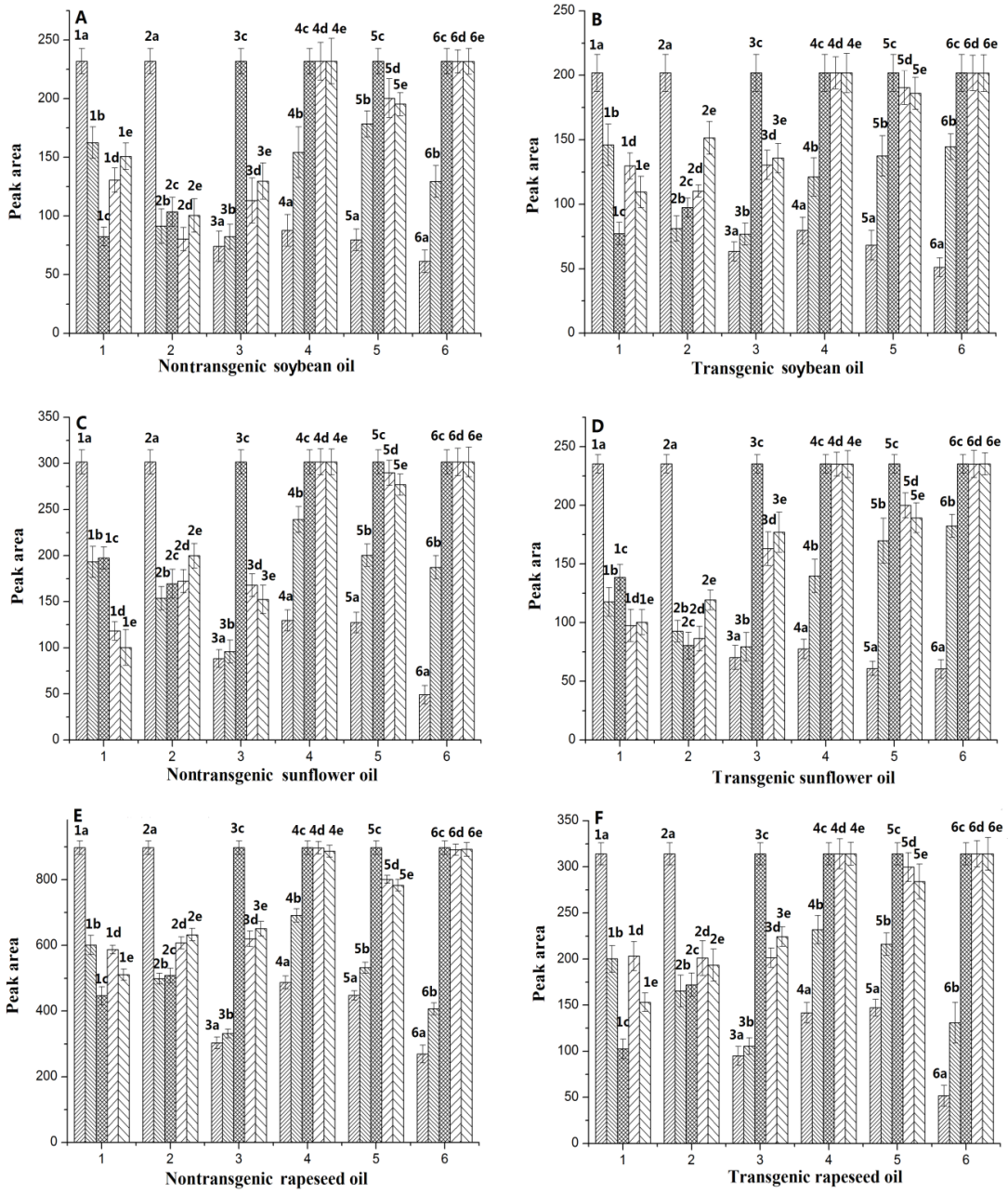


Figure S1. Effect of extraction solvents, co-solvents, catalysts, DDCETS volume, extraction-derivatization temperature and time (total peak areas of derivatives) for non-transgenic bean oil (A), transgenic bean oil (B), non-transgenic sunflower oil (C), transgenic sunflower oil (D), non-transgenic rapeseed oil (E) and transgenic rapeseed oil (F). 1 for extraction solvents: 1a (methanol), 1b (ACN), 1C (chloroform), 1d (ethanol), 1e (DMF) ; 2 for co-solvents: 2a (DMF), 2b (ethyl acetate), 2c (acetone), 2d (DMSO), 2e (chloroform); 3 for catalysts: 3a (pyridine), 3b (2-methylpyridine), 3c (K_2CO_3), 3d (Na_2CO_3), 3e ($K_2C_2O_4$); 4 for DDCETS volume: 4a (0.6 mL), 4b (0.8 mL), 4c (1.0 mL), 4d (1.2 mL), 4e (1.4 mL); 5 for extraction-derivatization temperature: 5a (80 ◦C), 5b (100 ◦C), 5c (130 ◦C), 5d (135 ◦C), 5d (140 ◦C); 6 for extraction-derivatization time: 6a (15 min), 6b (25 min), 6c (35min), 6d (45 min), 6e (55 min), with standard deviations included.

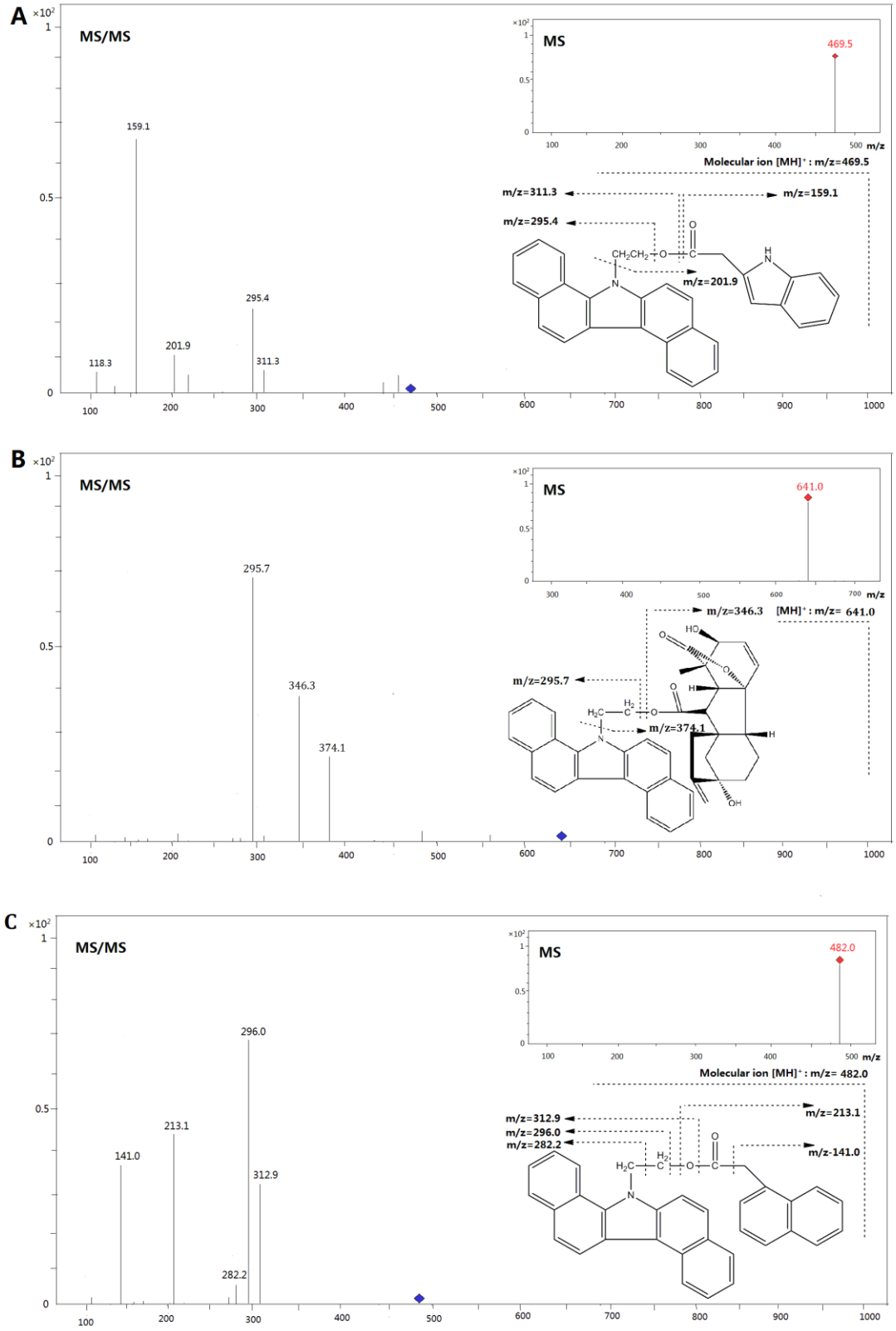


Figure S2. Typical mass spectrum and cleavage mode for DDCETS–IAA (A), DDCETS–GA_3 (B) and DDCETS-1-NAA (C).

Table S1

The recovery and matrix effect of GA_3 (gibberellin A_3),IAA(indole-3-aceticacid),IPA(indole-3-propionic acid),IBA(indole-3-butyric acid),1-NAA(1-naphthaleneacetic acid) and 2-NAA(2-naphthaleneacetic acid) in the six oilsamples (% *n*=6)..

PGRs	Matrix effects (%)[a]																	
Spiked ($ng\ mL^{-1}$)	Transgenic soybean oil			Nontransgenicsoybean oil			Transgenicsunflower oil			Nontransgenic sunflower oil			Transgenic rapeseed oil			Nontransgenic rapeseed oil		
	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100
GA_3	97.6	95.5	100.1	98.3	101.7	100.5	97.1	96.7	100.6	101.3	99.7	99.8	98.3	99.4	101.2	97.8	101.2	98.5
IAA	101.1	101.6	100.8	98.7	102.2	101.7	102.5	98.9	102.1	103.1	99.6	103.2	98.6	101.4	100.8	98.4	100.5	101.1
IPA	102.9	98.7	97.9	98.1	102.9	102.3	101.4	102.6	98.7	98.2	97.4	99.6	103.9	103.4	101.8	102.5	101.7	98.9
IBA	98.7	102.1	102.3	100.5	98.7	101.0	98.9	102.1	99.6	102.5	101.0	98.3	103.5	101.8	103.1	103.5	97.0	100.8
1-NAA	101.1	102.0	101.9	98.5	102.1	102.6	102.2	100.8	100.4	102.3	102.0	102.9	98.7	102.1	101.5	99.3	101.6	101.7
2-NAA	101.3	99.5	99.7	102.3	102.0	101.4	102.4	100.5	100.1	100.8	102.1	102.0	102.3	101.8	99.9	101.4	102.6	100.3
PGRs	Recovery (%)[b]																	
Spiked ($ng\ mL^{-1}$)	Transgenic soybean oil			Nontransgenicsoybean oil			Transgenicsunflower oil			Nontransgenic sunflower oil			Transgenic rapeseed oil			Nontransgenic rapeseed oil		
	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100
GA_3	96.1	96.2	99.9	97.3	98.4	97.3	99.7	98.1	98.7	96.1	97.0	100.2	97.8	96.3	98.3	98.8	98.2	96.7
IAA	103.2	101.4	99.0	99.3	102.5	97.9	100.6	97.9	102.3	103.2	98.7	98.9	102.4	101.7	103.1	101.1	104.4	103.5
IPA	98.2	97.6	97.8	97.9	100.1	99.6	97.3	101.1	99.6	99.0	102.6	101.9	97.8	98.0	101.0	102.6	101.1	102.0
IBA	98.5	101.2	98.9	101.2	104.0	102.9	98.7	97.9	100.5	102.2	101.9	103.3	101.8	103.0	98.7	99.9	99.0	98.9
1-NAA	101.4	101.7	102.5	97.9	98.0	102.1	101.6	102.0	98.7	101.3	97.6	103.0	103.1	103.7	101.9	98.9	98.7	99.0
2-NAA	98.1	99.4	100.1	99.1	100.2	100.4	102.2	101.7	98.2	98.7	98.9	100.7	97.8	98.5	101.0	101.9	97.6	97.9

[a] The matrix effect was evaluated following: matrix effect (%) = $S_p/S_s \times 100\%$, where, the S_p was the peak area of the spiked post-extraction sample and the S_s was the peak area of the known QC (quality control) solution.

[b] Recovery was calculated with the equation: $(S_2 - S_1)/S_0 \times 100\%$, where S_0, S_1 and S_2 were the peak area of quality control solution spiked, peak area of samples, and peak area of samples spiked with quality control solution, respectively.

Table S2

The stability evaluation of GA_3 (gibberellin A_3), IAA (indole-3-acetic acid), IPA (indole-3-propionic acid), IBA (indole-3-butyric acid), 1-NAA (1-naphthaleneacetic acid) and 2-NAA (2-naphthaleneacetic acid) and corresponding derivatives at three QC levels (*n*=6).

Compound	Short-term		long-term		Storage		Freeze–thaw	
spiked (ng mL^{-1})	Mean ± SD	RE%	Mean ± SD	RE%	Mean ± SD	RE%	Mean ± SD	RE%
GA_3								
100	90.1±8.97	-9.91	87.3±7.45	-12.67	89.7±7.92	-10.3	87.6±8.01	-12.4
500	470.2±19.69	-5.96	453.5±28.34	-9.30	462.9±18.98	-7.42	445.1±39.15	-10.98
1000	956.9±36.77	-4.31	920.5±58.32	-7.95	935.2±45.01	-6.48	924.9±45.22	-7.51
GA_3-derivative								
100	97.3±1.13	-2.70	93.7±4.29	-6.30	96.1±7.02	-3.90	94.3±4.98	-5.70
500	490.1±5.79	-1.98	480.9±6.28	-3.82	487.3±5.66	-2.54	476.9±10.80	-4.62
1000	993.5±5.21	-0.65	980.9±9.44	-1.91	987.8±10.12	-1.22	975.5±9.66	-2.45
IAA								
100	96.4±7.31	-3.60	94.2±6.99	-5.80	103.9±7.82	3.90	90.5±11.05	-9.50
500	482.1±10.5	-3.58	469.7±9.98	-6.06	487.0±13.91	-2.60	466.4±13.05	-6.72
1000	1033.1±5.91	3.31	945.4±17.31	-5.46	968.5±6.31	-3.15	947.9±7.12	-5.21
IAA-derivative								
100	101.5±7.22	1.50	97.4±7.13	-2.60	98.5±8.03	-1.50	95.9±7.22	-4.10
500	497.6±5.97	-0.48	490.3±16.69	-1.94	495.6±6.19	-0.88	488.5±17.18	-2.30
1000	997.4±8.26	-0.26	1022.7±1.11	2.27	991.6±8.64	-0.84	980.3±6.11	-1.97
IPA								
100	94.5±7.17	-5.50	92.1±9.02	-7.90	95.1±4.66	-4.90	90.8±9.56	-9.20
500	477.3±20.51	-4.54	456.9±29.10	-8.62	470.4±21.71	-5.92	467.5±29.62	-6.50
1000	981.3±12.39	-1.87	973.9±20.08	-2.61	980.7±21.07	-1.93	978.6±20.46	-2.14
IPA-derivative								
100	98.7±5.82	-1.30	94.2±8.13	-5.80	97.9±8.55	-2.10	94.8±5.19	-5.20
500	503.6±4.29	0.72	480.4±12.07	-3.92	485.3±9.94	-2.94	478.2±17.34	-4.36
1000	1003.4±7.55	0.34	986.9±11.03	-1.31	990.8±12.75	-0.92	980.3±13.17	-1.97
IBA								
100	95.1±3.08	-4.90	89.3±14.99	-10.70	93.9±5.12	-6.10	90.7±6.63	-9.30
500	507.5±6.19	1.50	477.2±19.56	-4.56	487.5±17.18	-2.50	486.0±10.01	-2.80
1000	983.7±11.06	-1.63	977.3±20.59	-2.27	980.3±12.91	-1.97	978.3±20.77	-2.17
IBA-derivative								
100	98.2±7.51	-1.80	90.1±10.33	-9.90	95.1±4.35	-4.90	94.2±7.13	-5.80
500	502.1±6.67	0.42	488.3±6.43	-2.34	493.6±7.18	-1.28	487.3±5.51	-2.54
1000	1007.7±4.92	0.77	983.8±20.79	-1.62	989.7±21.49	-1.03	980.2±22.38	-1.98
1-NAA								
100	103.4±4.9	3.40	88.2±8.3	-11.8	96.8±2.0	-3.20	94.6±3.9	-5.40
500	489.0±18.9	-2.20	477.2±14.8	-4.56	477.7±12.3	-4.46	470.7±14.5	-5.86
1000	959.2±27.0	-4.08	956.5±30.9	-4.35	957.2±28.9	-4.28	950.5±31.9	-4.95
1-NAA-derivative								
100	97.9±4.1	-2.10	96.7±4.0	-3.30	98.2±0.5	-1.80	96.3±2.1	-3.70
500	496.4±12.9	-0.72	478.4±17.4	-4.32	495.0±12.5	-1.00	472.3±15.2	-5.54

1000	970.4±25.6	-2.96	959.8±35.0	-4.02	968.4±24.9	-3.16	953.6±35.0	-4.64
2-NAA								
100	97.0±3.4	-2.01	95.4±5.3	-4.60	103.5±1.0	3.50	104.7±1.5	4.70
500	482.7±13.0	-3.46	478.3±16.9	-4.34	480.4±14.9	-3.92	462.7±15.9	-7.46
1000	1046.6±59.0	4.66	1046.4±21.0	4.64	969.9±27.9	-3.01	961.9±20.6	-3.81
2-NAA-derivative								
100	100.1±7.9	0.10	97.1±4.4	-2.90	100.6±0.8	0.60	97.7±1.1	-2.30
500	479.2±13.5	-2.78	471.3±15.9	-5.74	472.8±13.2	-5.44	467.3±13.6	-6.54
1000	978.9±18.9	-2.11	970.0±28.0	-3.00	972.0±26.1	-2.80	1031.0±18.0	3.10

Table S3

Comparison of the proposed method for detection of PGRs in samples.

Samples	Sample amount	Analytes	Operations	Pretreatment Time [a]	Recovery	LOD [b] (ng mL^{-1})	Ref./this work
Plant tissues	0.5g 0.25g	ABA, IAA, JA	LE-HPLC-ESI-MS/MS	>2.5h	85%-93%	38-2512	[17]
Grape samples	2.0 g	IAA ,IBA ,NAA, GA_3 ,2IP	SPE-HPLC–MS/MS	>3h	82.5–105.4 %	0.08-1.2	[18]
Vegetable samples	150g	NAA,NOA,IAA, IBA,IPA	LLE-CE-UV	>2.5h	91-118.0%	450-1040	[19]
Fruit samples	0.5g	GA_3,IAA, ABA, JA, IBA, NAA,2,4-D	LE-CE–LIF	>12h	90.7 - 106.1%	0.423-2.32	[20]
Tobacco root and Arabidopsis thaliana seedling	300 mg	7PGRs (ACC, SA,IAA,etc.)	SPE-GC–MS	>2.5h	_	50-5000	[21]
Wild-type and GM plants	1.5g	IAA, S-ABA, iP, iPA, Z, ZR	SPE-GC–MS SPE-HPLC–MS/MS	>12h	HPLC–MS/MS (87–98%), GC–MS (53–89%).	HPLC–MS/MS1.5-15 GC–MS 1.5-30	[22]
Fresh plant tissue	50 mg	18 phytohormones (ICA, IAA, IBA, etc.)	LLME-HPLC–ESI–MS/MS	>3h	85-98%	0.1-1	[23]
Plant samples	1g	JA,IAA,IPA,IBA,1-NAA,2-NAA,GA	LE-HPLC -FLD	>3h	94-104%	0.34–0.73	[24]
Tobacco leaf	1g	ABA	LE-CE–LIF	>12h	97%	0.264	[25]

Soil samples	3.0 g	IAA	LE-GPU-SWV	>3.5h	95.1±2.7%	26	[26]
Plant materials	0.022-1.214g	24 phytohormones (IAA, ABA, GA, etc.)	SPE-HPLC–ESI–MSn	>12h	22.56±1.29%-95.64±2.94%	0.325-136	[27]
Natural coconut juice	-	SA, IAA ABA, JA	HF-LLLME-HPLC-UV	>3h	88.3–119.1%	0.9-8800	[28]
Lemna minor L.	1g	JA	SPE-LC-FLD	>3.5h	63-79%	_	[29]
Plant materials	50mg	ABA	SPE-HPLC–ESI–MS	>3.5h	91±8%	0.38	[30]
Rice leaves	5 mg	11 phytohormones(IAA, GA, IBA, etc.)	SPE-Nano-LC–ESI-Q-TOF-MS	>1.5d	88.3-104.3%.	0.00105-0.1224	[31]
Apples and tomatoes	5g	6 PGRs	DSPE-HPLC/MS/MS	>2.5h	71.7-98.1%	0.01-2.6	[32]
Oilseed rape samples	0.1 g	IAA,ABA,GA_3,IBA, JA,SA	SPE-HPLC- ESI- MS /MS	>3h	67.03-119.83%	0.005-0.2	[33]
Plant samples	50–100 mg	17PGRs (SA, IAA, ABA, etc.)	LLME-LC–ESI–MS/MS	>3h	>95%	0.001-1	[34]
Pears	10g	IAA,IPA,2,4-D, 1-NAA,2-NOA, MNAA	MAE-LC-ESI-MS	>3h	78.9-118.0%	3 - 19	[35]
Vegetable Samples	0.5g	IBA,NAA,2,4-D	LE-HPLC-FLD	>12h	94.2-102.4%	0.49-1.5	[36]
Soybean leaves	500 mg	JA	UAE-HPLC-FLD	>3h	95-104%	0.24	[37]
Oil samples	3g	GA_3,IAA,IPA,IBA,1-NAA,2-NAA	MAED-HPLC-FLD	< 1.5h	96.1-104.4%	0.37-1.36	This work

[a] The total time of sample pretreatment, separation and detection.

[b] LOD: limit of detection (at the signal-to-noise ratio of 3:1).

-: not found.

Table S4

Contents of GA_3 (gibberellin A_3), IAA (indole-3-acetic acid),IPA (indole-3-propionic acid), IBA (indole-3-butyric acid), 1-NAA (1-naphthaleneacetic acid) and 2-NAA (2-naphthaleneacetic acid) in four batches of oil samples (*n*=6).

Samples	PGRs	1[a]		2[a]		3[a]		4[a]	
		Average[a]	RSD[b]	Average[a]	RSD[b]	Average[a]	RSD[b]	Average[a]	RSD[b]
		μg/g	%	μg/g	%	μg/g	%	μg/g	%
Nontransgenic rapeseed oil	GA_3	8.862	0.9	8.875	1.3	8.851	1.5	8.858	0.8
	IAA	2.931	2.3	2.928	1.7	2.915	1.6	2.936	2.1
	IPA	-	-	-	-	-	-	-	-
	IBA	3.801	2.3	3.783	1.5	3.804	2.8	3.787	1.3
	1-NAA	8.294	2.1	8.288	1.3	8.297	1.8	8.288	2.2
	2-NAA	10.848	2.7	10.867	2.3	10.852	2.1	10.859	1.7
Transgenic rapeseed oil	GA_3	5.894	2.5	5.907	1.9	5.900	2.5	5.899	2.9
	IAA	4.827	1.3	4.834	2.1	4.830	1.2	4.825	1.7
	IPA	0.032	1.1	0.029	1.4	0.031	0.7	0.032	1.8
	IBA	2.875	2.6	2.879	2.7	2.867	1.3	2.873	1.6
	1-NAA	-	-	-	-	-	-	-	-
	2-NAA	0.031	1.7	0.033	1.9	0.036	1.3	0.035	1.9
Nontransgenicsoybean oil	GA_3	3.304	1.9	3.307	2.3	3.298	1.4	3.301	1.7
	IAA	3.155	1.1	3.149	1.4	3.153	0.7	3.157	1.8
	IPA	0.018	2.0	0.019	1.6	0.015	1.8	0.018	2.5
	IBA	1.905	2.3	1.909	1.7	1.912	1.4	1.907	1.9
	1-NAA	0.040	1.7	0.044	1.6	0.039	1.1	0.043	2.1
	2-NAA	0.041	2.5	0.038	2.1	0.043	1.8	0.038	2.4
Transgenic soybean oil	GA_3	3.345	0.4	3.337	1.0	3.342	1.8	3.344	2.3
	IAA	1.361	2.3	1.363	0.9	1.366	1.9	1.360	2.4
	IPA	-	-	-	-	-	-	-	-
	IBA	2.165	1.8	2.163	1.3	2.157	2.1	2.159	1.3
	1-NAA	-	-	-	-	-	-	-	-
	2-NAA	0.014	1.0	0.017	2.4	0.018	1.3	0.019	1.2
Nontransgenic sunflower oil	GA_3	7.664	2.3	7.667	1.8	7.656	2.1	7.658	1.4
	IAA	2.160	1.9	2.165	2.8	2.157	1.5	2.161	1.4
	IPA	-	-	-	-	-	-	-	-
	IBA	2.877	1.3	2.883	1.9	2.882	1.6	2.881	0.7
	1-NAA	0.036	1.2	0.034	1.9	0.032	2.0	0.035	1.0
	2-NAA	0.043	0.8	0.045	0.9	0.040	1.2	0.042	1.1
Transgenic sunflower oil	GA_3	3.534	1.1	3.528	1.7	3.533	0.5	3.531	1.2
	IAA	3.064	1.7	3.063	1.8	3.057	1.1	3.059	1.4
	IPA	-	-	-	-	-	-	-	-
	IBA	2.270	1.5	2.273	1.9	2.267	1.0	2.271	1.7
	1-NAA	-	-	-	-	-	-	-	-
	2-NAA	0.023	1.1	0.025	2.0	0.027	1.2	0.023	1.4

[a] Four batches of six oil samples were all purchased from a supermarket in Qufu (Shan dong province, China).

[b] The average contents of GA_3, IAA, IPA, IBA, 1-NAA and 2-NAA in oil samples.

[c] The relative standard deviation (n=6).

- Not found.