

## Supplementary data

Figure S1. High collision energy ESI-MS spectra of peaks 51(A), 54(B), 59(C), 75(D), 80(E), and 83(F).

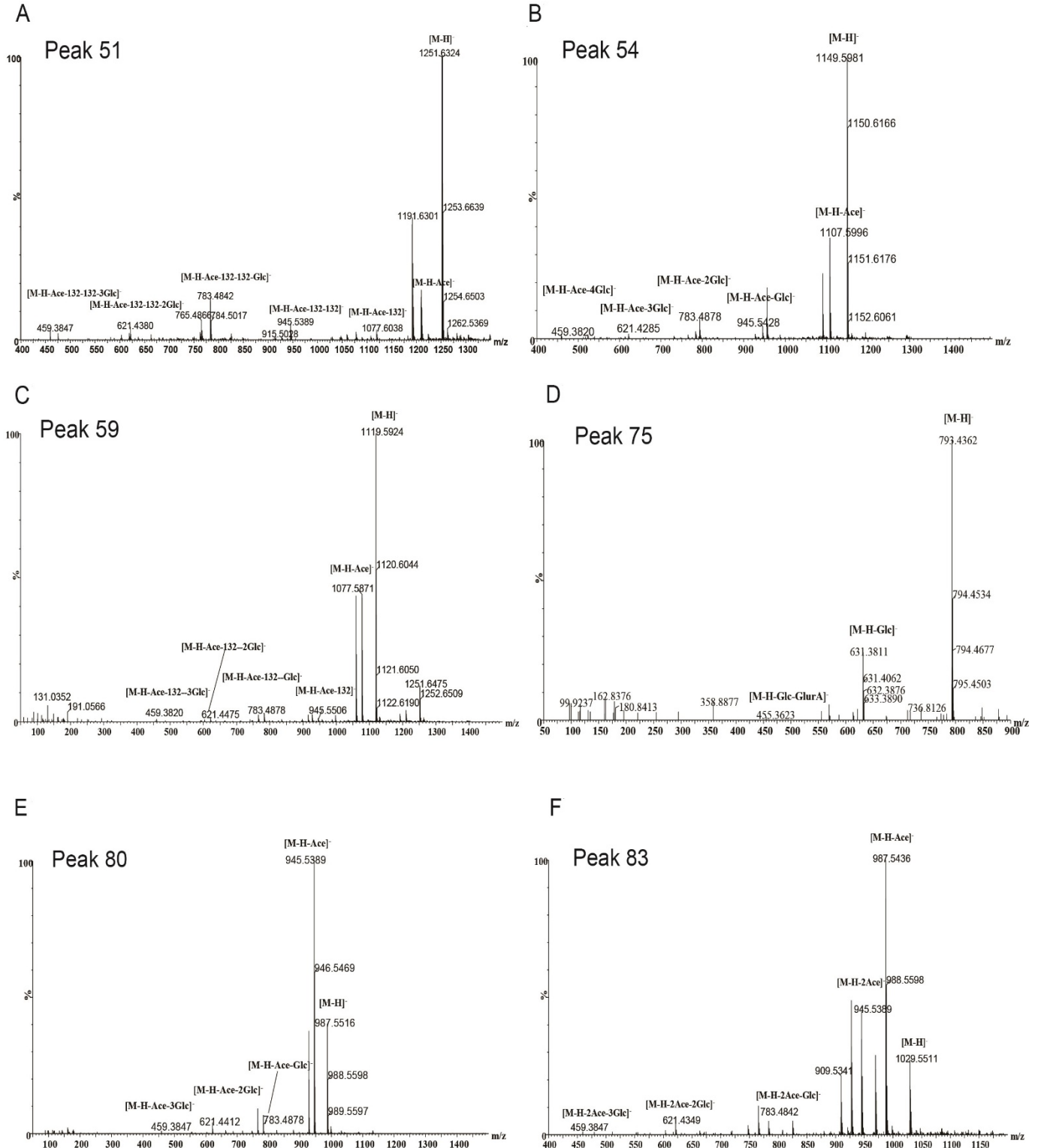
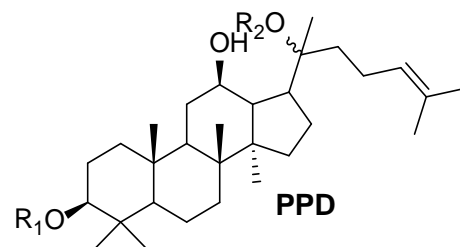


Table S1-1. Chemical structures of the detected compounds in different parts of *P. ginseng* root (PPD-type).

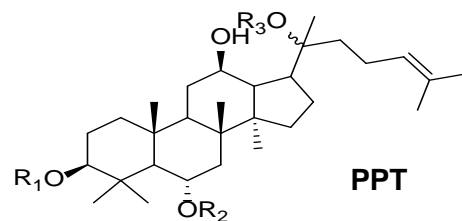


No	Name	R1	R2
38/84	malnoylfloralginsenosides Rd <sub>6</sub>	Glc(2,1)Glc(6)-Mal	Glc(6)-Mal
38/84	$\beta$ -D-Glucopyranoside, (3 $\beta$ ,12 $\beta$ )-20-( $\beta$ -D-glucopyranosyloxy)-12-hydroxydammar-24-en-3-yl 2-O-[6-O-(2-carboxyacetyl)- $\beta$ -D-glucopyranosyl]-, 6-(hydrogen propanedioate)	Glc-[6-Mal]-(2,1)Glc-[6-Mal]	Glc
42	Notoginsenoside R <sub>4</sub>	Glc(2,1)Glc	Glc(6,1)Glc(3,1)Xyl
44/52	Yesaninoside J	Glc-[6-Ace]-(2,1)Glc	Glc(6,1)Glc(6,1)Xyl
45	malonyl-ginsenoside Ra <sub>3</sub> / malonyl-notoginsenoside R <sub>4</sub>	Glc(2,1)Glc(6)-Mal	Glc(6,1)Glc(3,1)Xyl/Glc(6,1)Glc(6,1)Xyl
48	Ginsenoside Ra <sub>2</sub>	Glc(2,1)Glc	Glc(6,1)Ara( <i>f</i> 2,1) Xyl
49	Ginsenoside Ra <sub>3</sub>	Glc(2,1)Glc	Glc(6,1)Glc(3,1)Xyl
50	Rb <sub>1</sub>	Glc(2,1)Glc	Glc(6,1)Glc
51/58/66/70/72/73	Ra <sub>5</sub>	Glc(2,1)Glc(6)-Ace	Glc(6,1)Ara( <i>p</i> 4,1)Xyl

51/58/66/70/72/73	(3 $\beta$ ,12 $\beta$ )-3-[[2-O-(6-O-Acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl]oxy]-12-hydroxydammar-24-en-20-yl O- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-arabinopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside	Glc(2,1)Glc(6)-Ace	Glc(6,1)Ara( <i>p</i> 2,1)Xyl
56	Rc	Glc(2,1)Glc	Glc(6,1)Ara( <i>f</i> )
57/62	Ra <sub>1</sub>	Glc(2,1)Glc	Glc(6,1)Ara( <i>p</i> 4,1)Xyl
54/61/64/74	Quinquenoside R <sub>1</sub>	Glc(2,1)Glc(6)-Ace	Glc(6,1)Glc
54/61/64/74	(3 $\beta$ ,12 $\beta$ )-20-[[6-O-(6-O-Acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranosyl]oxy]-12-hydroxydammar-24-en-3-yl 2-O- $\beta$ -D-glucopyranosyl- $\beta$ -D-glucopyranoside	Glc(2,1)Glc	Glc(6,1)Glc(6)-Ace
55	malonyl-ginsenoside Rb <sub>1</sub>	Glc(2,1)Glc(6)-Mal	Glc(2,1)Glc
60	malonyl-ginsenoside Rc	Glc(2,1)Glc(6)-Mal	Glc(6,1)Ara( <i>f</i> )
63	Rb <sub>2</sub>	Glc(2,1)Glc	Glc(6,1)Ara( <i>p</i> )
65	Rb <sub>3</sub>	Glc(2,1)Glc	Glc(6,1)Xyl
59/67/69/71/76/77/8 2	Rs <sub>1</sub>	Glc(2,1)Glc(6)-Ace	Glc(6,1)Ara( <i>p</i> )
59/67/69/71/76/77/8 2	Rs <sub>2</sub>	Glc(2,1)Glc(6)-Ace	Glc(6,1)Ara( <i>f</i> )
59/67/69/71/76/77/8 2	Pseudoginsenoside F <sub>8</sub>	Glc-[6-Ace]-(2,1)Glc	Glc(6,1)Ara( <i>p</i> )
68	malonyl-ginsenoside Rb <sub>2</sub>	Glc(2,1)Glc(6)-Mal	Glc(6,1)Ara( <i>p</i> )
78	malonyl-ginsenoside Rb <sub>3</sub>	Glc(2,1)Glc(6)-Mal	Glc(6,1)Xyl
79	Rd	Glc(2,1)Glc	Glc

80/81/86/89/93	Pseudoginsenoside Rc <sub>1</sub>	Glc(2,1)Glc(6)-Ace	Glc
80/81/86/89/93	Quinquenoside III	Glc-[6-Ace]-(2,1)Glc	Glc
80/81/86/89/93	$\beta$ -D-Glucopyranoside, (3 $\beta$ , 12 $\beta$ )-3-( $\beta$ -D-glucopyranosyloxy)-12-hydroxydammar-24-en-20-yl 6-O-(6-O-Acetyl- $\beta$ -D-glucopyranosyl)- (9CI)	Glc	Glc(6,1)Glc(6)-Ace
85	Gyenoside XVII	Glc	Glc(6,1)Glc
87	Ginsenoside Ra <sub>6</sub> /Quinquenoside II	Glc(2,1)Glc(6)-But	Glc(6,1)Glc
88	malonyl-ginsenoside Rd	Glc(2,1)Glc(6)-Mal	Glc
91	Ginsenoside Ra <sub>7</sub>	Glc(2,1)Glc(6)-But	Glc(6,1)Ara( <i>p</i> )
92	Gyenoside IX	Glc	Glc(6,1)Xyl
94/98	Ginsenoside Ra <sub>8</sub> /Ginsenoside Ra <sub>9</sub>	Glc(2,1)Glc(3)-But/Glc(2,1)Glc(6)- But	Glc(6,1)Ara( <i>f</i> )
96	Quinquenoside I	Glc(2,1)Glc(6)-But	Glc
97	(20S)-Ginsenoside Rg <sub>3</sub>	Glc(2,1)Glc	H
99	20(S)-Ginsenoside Rs <sub>3</sub>	Glc(2,1)Glc(6)-Ace	H
100	(20R)-Ginsenoside Rg <sub>3</sub>	Glc(2,1)Glc	H
101	(20R)-Ginsenoside Rs <sub>3</sub>	Glc(2,1)Glc(6)-Ace	H
103	20(S)-Ginsenoside Rh <sub>2</sub>	Glc	H
104	20(R)-Ginsenoside Rh <sub>2</sub>	Glc	H

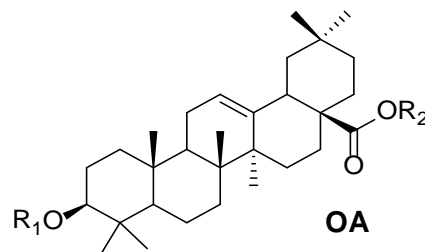
Table S1-2. Chemical structures of the detected compounds in different parts of *P. ginseng* root (PPT-type).



No	Name	R1	R2	R3
7/11/15	Ginsenoside Re <sub>1</sub>	H	Glc	Glc(3,1)Glc
7/11/15	Ginsenoside Re <sub>2</sub>	H	Glc(3,1)Glc	Glc
7/11/15	Ginsenoside Re <sub>3</sub>	H	Glc	Glc(4,1)Glc
8/10	Ginsenoside Re <sub>4</sub>	H	Glc	Glc(6,1)Ara(f)
9	20-O-Glucosylginsenoside Rf	H	Glc(2,1)Glc	Glc
12/17	Yesaninoside E	H	Glc(2,1)Rha	Glc(6,1)Glc
13	Floralginsenoside M/Floralginsenoside N	H	Glc(2,1)Rha	Glc(6,1)Ara(f)/Glc(6,1)Ara(p)
14	Notoginsenoside R <sub>1</sub>	H	Glc(2,1)Xyl	Glc
18/27/33/36/37	Vinaginsenoside R <sub>4</sub>	Glc(2,1)Glc	H	Glc
18/27/33/36/37	Notoginsenoside R <sub>3</sub>	H	Glc	Glc(6,1)Glc
18/27/33/36/37	Notoginsenoside R <sub>6</sub>	Glc	H	Glc(6,1)Glc
18/27/33/36/37	Notoginsenoside M	H	Glc(6,1)Glc	Glc
18/27/33/36/37	Notoginsenoside N	H	Glc(4,1)Glc	Glc
19	Rg <sub>1</sub>	H	Glc	Glc

20	Re	H	Glc(2,1)Rha	Glc
21/23/25	6'-O-Acetyl-ginsenoside Rg <sub>1</sub>	H	Glc(6)-Ace	Glc
22/24	6'''-O-Acetyl-ginsenoside Re	H	Glc(2,1)Rha	Glc(6)-Ace
28/31	Floralginsenoside P	Glc(2,1)Glc	H	Glc(6,1)Ara(p)
32/41	Yesanchinoside D	H	Glc(6)-Ace	Glc
39	Rf	H	Glc(2,1)Glc	H
40	Ginsenoside Re <sub>6</sub>	H	Glc	Glc(6)-But
40	Koryoginsenoside R <sub>1</sub>	H	Glc(6)-But	Glc
43	Notoginsenoside R <sub>2</sub>	H	Glc(2,1)Xyl	H
46	Rg <sub>2</sub>	H	Glc(2,1)Rha	H
47	20(R)-Ginsenoside Rh <sub>1</sub>	H	Glc	H

Table S1-3. Chemical structures of the detected compounds in different parts of *P. ginseng* root (OA-type).



No	Name	R1	R2
53	Ro	GlurA(2,1)Glc	Glc
75/95	Chikusetsusaponin Iva	GlurA	Glc

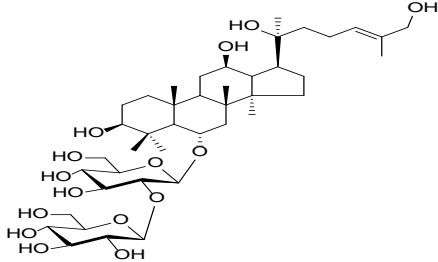
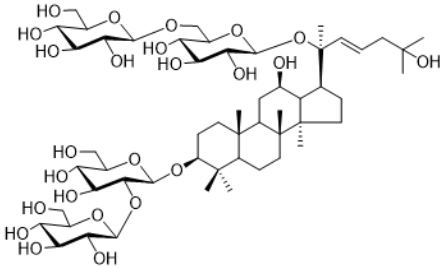
30

Pseudoginsenoside Rt<sub>1</sub>

GlurA(2,1)Xyl

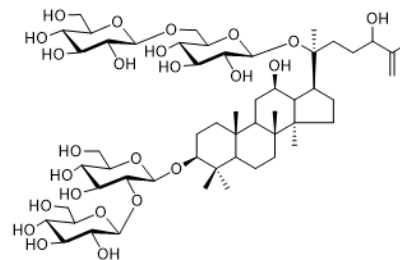
Glc

Table S1-4. Chemical structures of the detected compounds in different parts of *P. ginseng* root (others).

No	Name	Molecular structure
1/3/4/34	Ginsenoside Re <sub>5</sub> isomer	 <p>The structure shows a ginsenoside core with a complex sugar chain on the left and a side chain on the right. The side chain includes a double bond and a terminal hydroxyl group.</p>
5	Koryoginsenoside R <sub>2</sub>	 <p>The structure shows a ginsenoside core with a complex sugar chain on the left and a side chain on the right. The side chain includes a double bond and a terminal hydroxyl group.</p>

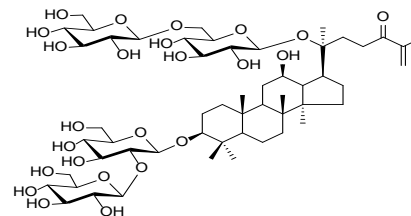
5

Ginsenoside V (24 $\beta$ )



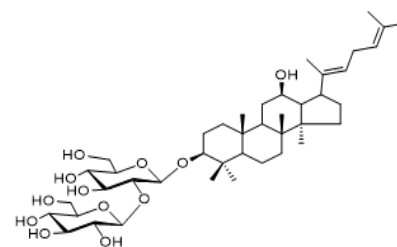
16

Notoginsenoside B



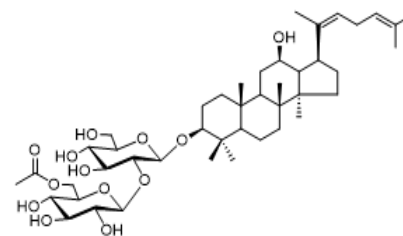
26

Ginsenoside Rg<sub>5</sub>



29

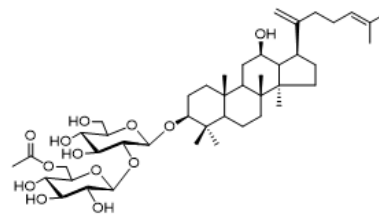
Ginsenoside Rs<sub>4</sub>





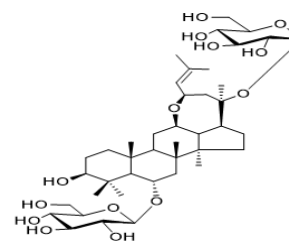
29

Ginsenoside R<sub>S5</sub>



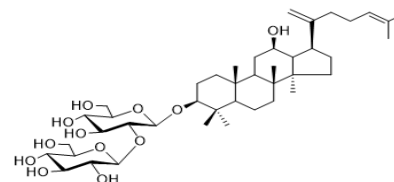
35

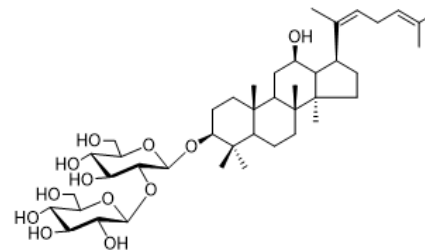
12,23-Eproxyginsenoside  
R<sub>G1</sub>



102/105

Ginsenoside R<sub>k1</sub>



Table S2 Detailed information of the tested *P. ginseng* whole root samples.

Sample number	Source	Growth year	Collection Time
HLJ-1	Sanjitai forest farm, Suiling County, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-2	Sanjitai forest farm, Suiling County, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-3	Sanjitai forest farm, Suiling County, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-4	Shuguang forest farm, Tieli City, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-5	Shuguang forest farm, Tieli City, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-6	Shuguang forest farm, Tieli City, Heilongjiang Province, China	4	2019.10–2019.11
HLJ-7	Baoqing County, Shuangyashan City, Heilongjiang Province, China	5	2019.10–2019.11
HLJ-8	Baoqing County, Shuangyashan City, Heilongjiang Province, China	5	2019.10–2019.11

HLJ-9	Baoqing County, Shuangyashan City, Heilongjiang Province, China	5	2019.10–2019.11
JL-1	Tonghua City, Jilin Province, China	4	2019.10–2019.11
JL-2	Tonghua City, Jilin Province, China	4	2019.10–2019.11
JL-3	Tonghua City, Jilin Province, China	4	2019.10–2019.11
JL-4	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-5	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-6	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-7	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-8	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-9	Taishang Town, Ji'an City, Jilin Province, China	4	2019.10–2019.11
JL-10	Jiayi Village, Qinghe Town, Ji'an City, Jilin Province, China	5	2019.10–2019.11
JL-11	Jiayi Village, Qinghe Town, Ji'an City, Jilin Province, China	5	2019.10–2019.11
JL-12	Jiayi Village, Qinghe Town, Ji'an City, Jilin Province, China	5	2019.10–2019.11
JL-13	Xintuntun Village, Xintun Town, Fusong County, Jilin Province, China	5	2019.10–2019.11
JL-14	Xintuntun Village, Xintun Town, Fusong County, Jilin Province, China	5	2019.10–2019.11

JL-15	Xintuntun Village, Xintun Town, Fusong County, Jilin Province, China	5	2019.10–2019.11
JL-16	Quanyang Town, Fusong County, Jilin Province, China	5	2019.10–2019.11
JL-17	Quanyang Town, Fusong County, Jilin Province, China	5	2019.10–2019.11
JL-18	Quanyang Town, Fusong County, Jilin Province, China	5	2019.10–2019.11
LN-1	Yongling Town, Xinbin County, Fushun City, Liaoning Province, China	4	2019.10–2019.11
LN-2	Yongling Town, Xinbin County, Fushun City, Liaoning Province, China	4	2019.10–2019.11
LN-3	Yongling Town, Xinbin County, Fushun City, Liaoning Province, China	4	2019.10–2019.11
LN-4	Dachuantou Town, Kuandian County, Dandong City, Liaoning Province, China	4	2019.10–2019.11
LN-5	Dachuantou Town, Kuandian County, Dandong City, Liaoning Province, China	4	2019.10–2019.11
LN-6	Dachuantou Town, Kuandian County, Dandong City, Liaoning Province, China	4	2019.10–2019.11
LN-7	Shizhuzi Village, Kuandian County, Dandong City, Liaoning Province, China	5	2019.10–2019.11
LN-8	Shizhuzi Village, Kuandian County, Dandong City, Liaoning Province, China	5	2019.10–2019.11
LN-9	Shizhuzi Village, Kuandian County, Dandong City, Liaoning Province, China	5	2019.10–2019.11

---