

Supporting Information

Untargeted metabolomics analysis to unveil the chemical markers for the differentiation among three *Gleditsia sinensis*-derived herbal medicines by ultra-high performance liquid chromatography/quadrupole time-of-flight mass spectrometry

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Fig. S4 Score plot of PCA based on the positive full-scan MS¹ data of 45 batches of *G. sinensis* and QC₂ samples. **GFA**: Gleditsiae Fructus Abnormalis; **GSF**: Gleditsiae Sinensis Fructus; **GS**: Gleditsiae Spina.

Fig. S5 The box chart showing the content difference of 46 characterized potential markers among GFA, GSF, and GS.

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Table S2 Detained information of the drug materials of three TCM species (Gleditsiae Spina, GS; Gleditsiae Sinensis Fructus, GSF; Gleditsiae Fructus Abnormalis, GFA) derived from *Gleditsia sinensis* analyzed in the current work.

Table S3 In-house library of *Gleditsia sinensis*.

Table S4 Detailed information of the potential differential components identified by comparing the chemical fingerprinting information of three TCM species derived from *Gleditsia sinensis*.

Table S5 The NMR data of compounds Saikachinoside A (DMSO-*d*₆ at 500 MHz) and Locustoside A (CD₃OD:D₂O=1:9 at 600 MHz).

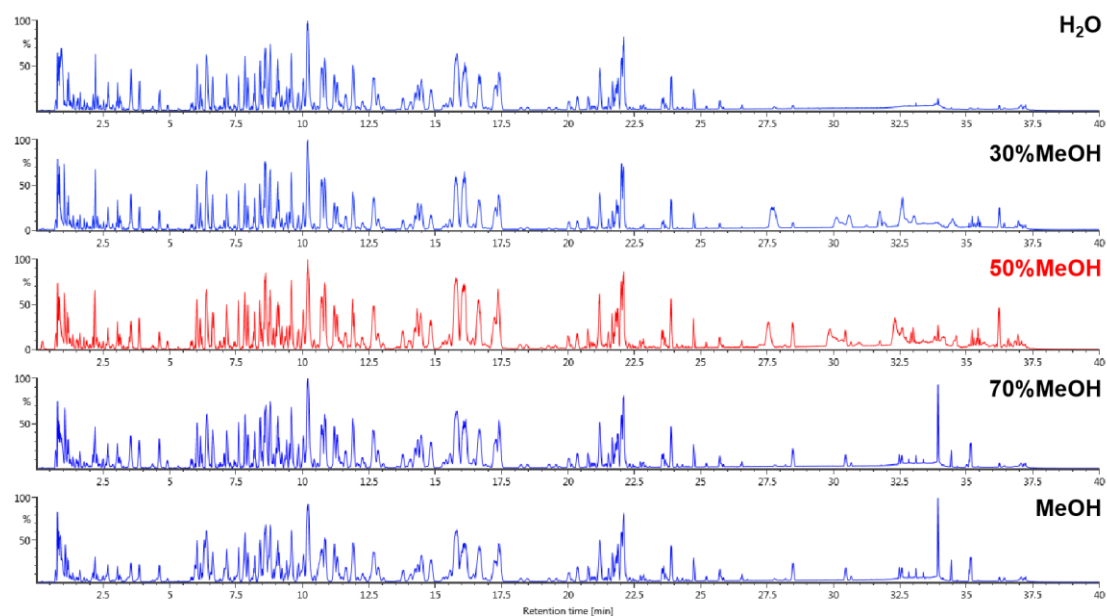


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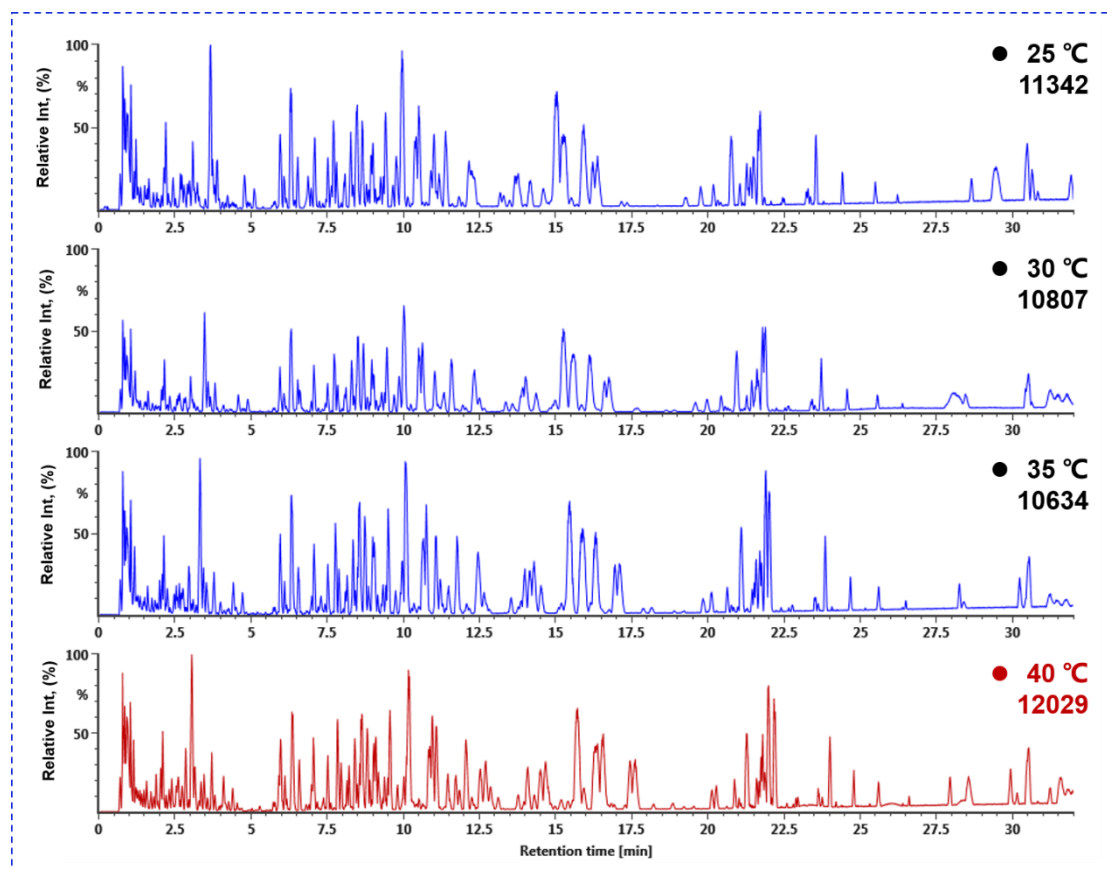


Fig. S2 Comparison of the column temperature for separating the multicomponents from QC₁ on the selected BEH C18 column.

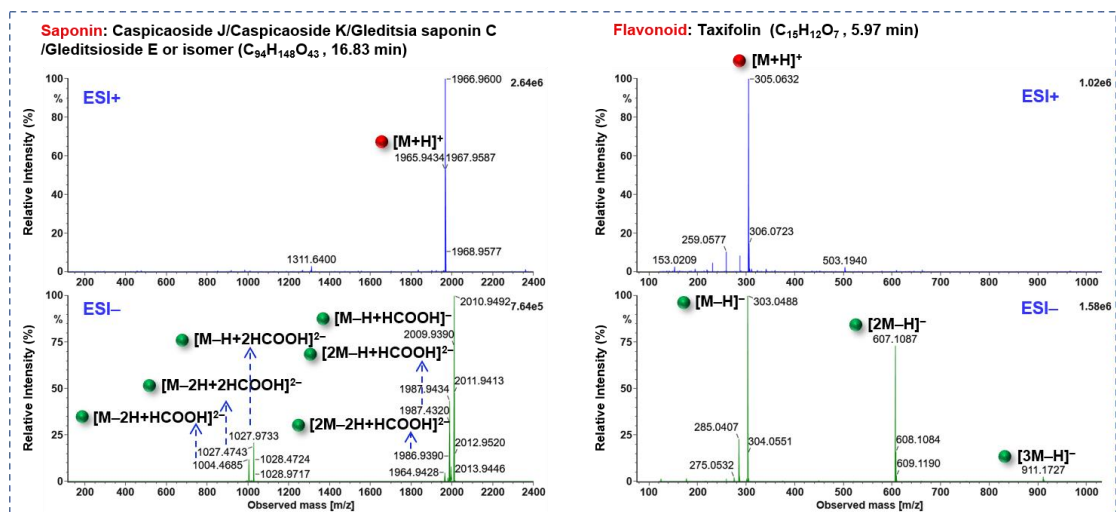


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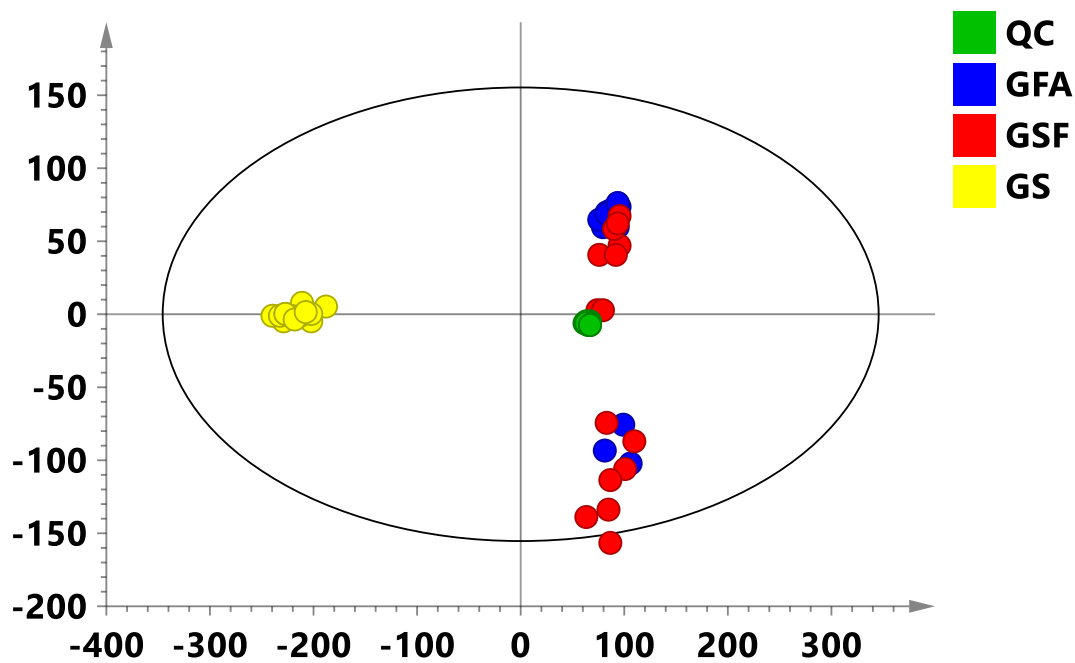
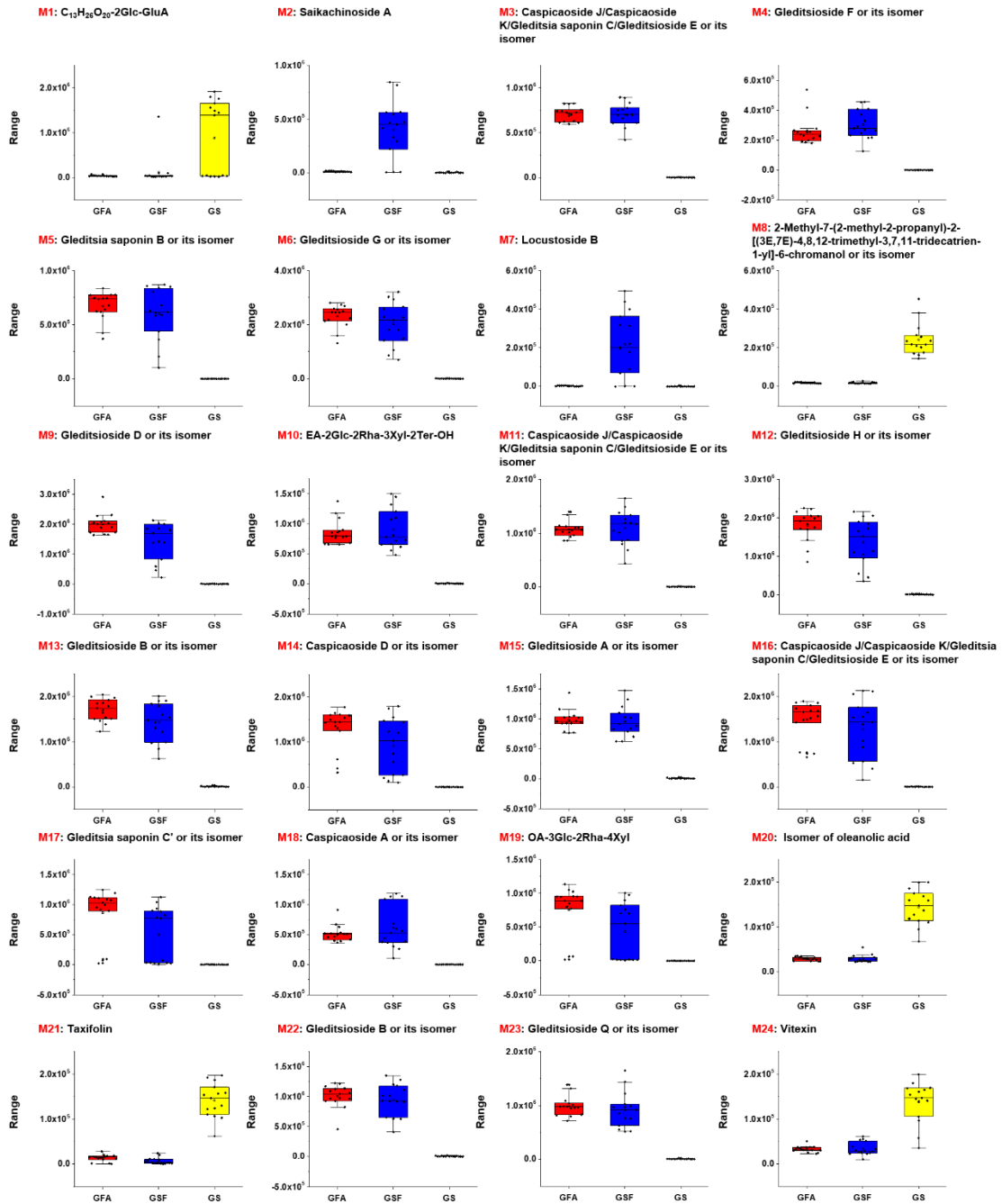


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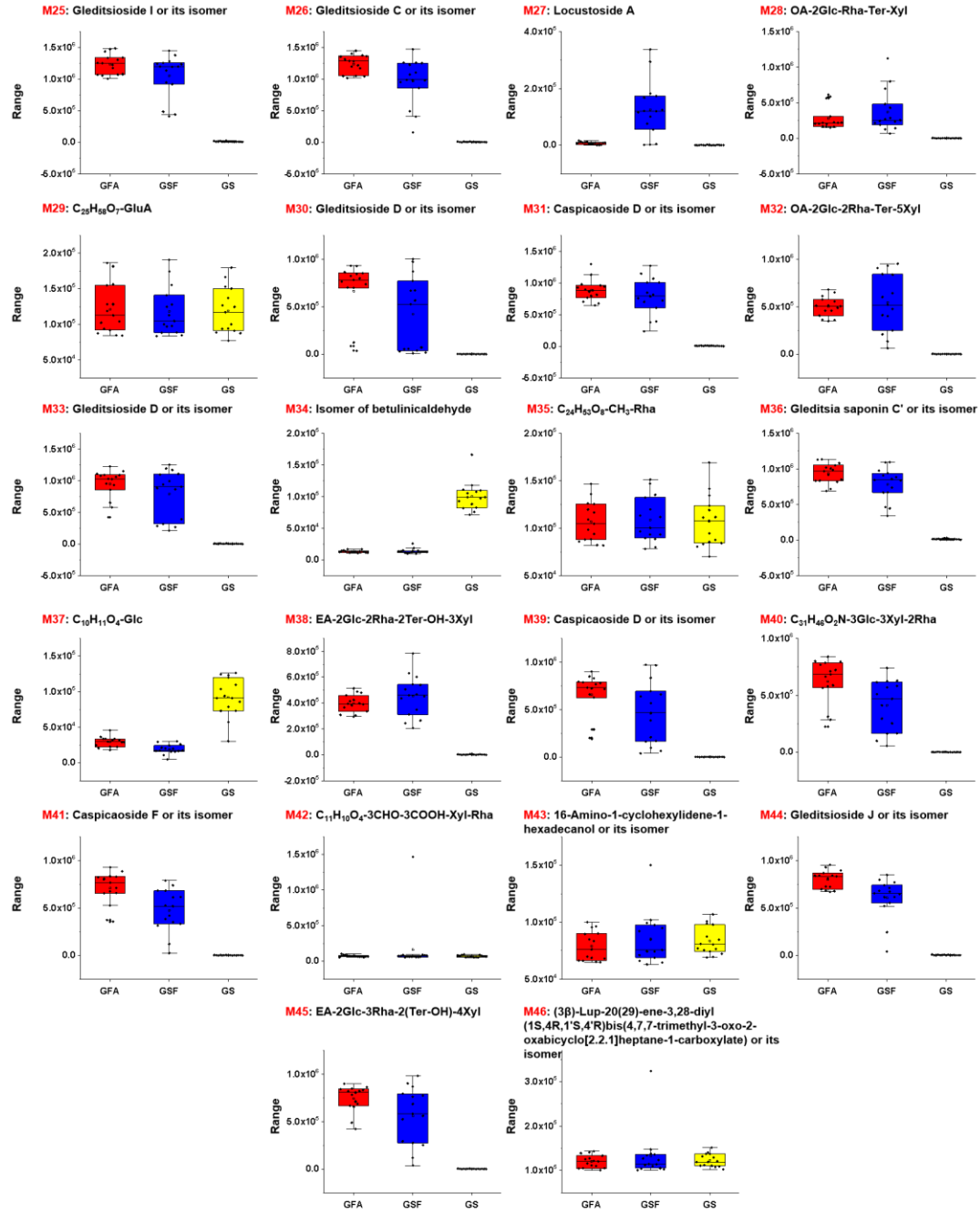


Fig. S5 The box chart showing the content difference of 46 characterized potential markers among GFA, GSF, and GS.

Table S1 Information of 26 reference compounds used this work for the chemical analysis of three TCM species derived from *Gleditsia sinensis*.

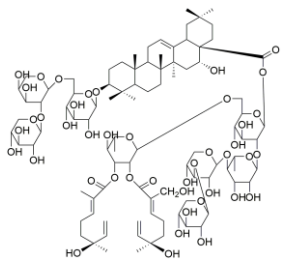
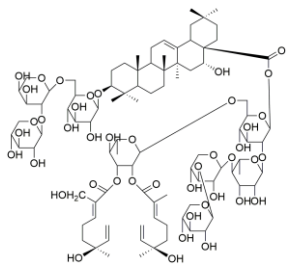
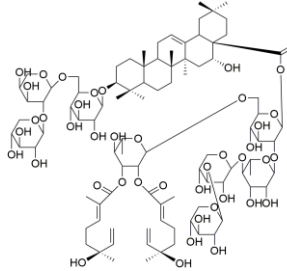
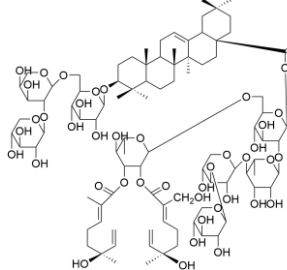
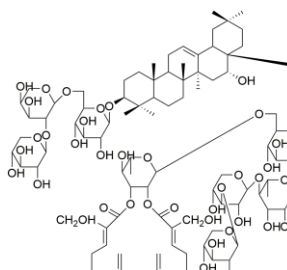
No.	Trivial name	Purity	M.F.	Exact Mass	Subclass
1	Isoquercitrin	98%	C ₂₁ H ₂₀ O ₁₂	464.0955	
2	Quercitrin	98%	C ₂₁ H ₂₀ O ₁₁	448.1006	
3	Cynaroside	98%	C ₂₁ H ₂₀ O ₁₁	448.1006	
4	Kaempferol	98%	C ₁₅ H ₁₀ O ₆	286.0477	
5	Quercetin (Meletin)	98%	C ₁₅ H ₁₀ O ₇	302.0427	
6	Apigenin	98%	C ₁₅ H ₁₀ O ₅	270.0528	
7	Dihydrokaempferol	98%	C ₁₅ H ₁₂ O ₆	288.0634	
8	Taxifolin	98%	C ₁₅ H ₁₂ O ₇	304.0583	Flavonoids
9	Eriodictyol	98%	C ₁₅ H ₁₂ O ₆	288.0634	
10	Licochalcone B	98%	C ₁₆ H ₁₄ O ₅	286.0841	
11	Isoliquiritigenin	98%	C ₁₅ H ₁₂ O ₄	256.0736	
12	Butein	98%	C ₁₅ H ₁₂ O ₅	272.0685	
13	Epicatechin	98%	C ₁₅ H ₁₄ O ₆	290.0790	
14	(-)-Catechin hydrate	97%	C ₁₅ H ₁₄ O ₆	290.0790	
15	Vitexin	98%	C ₂₁ H ₂₀ O ₁₀	432.1056	
16	Orientin	98%	C ₂₁ H ₂₀ O ₁₁	448.1006	
17	Betulin	98%	C ₃₀ H ₅₀ O ₂	442.3811	
18	Betulonic acid	98%	C ₃₀ H ₄₈ O ₃	456.3603	
19	Lupenone	98%	C ₃₀ H ₄₈ O	424.3705	Terpenes
20	Echinocystic acid	99%	C ₃₀ H ₄₈ O ₄	472.3553	
21	Daucosterol	98%	C ₃₅ H ₆₀ O ₆	576.4390	
22	Forsythin	99%	C ₂₇ H ₃₄ O ₁₁	534.2101	Lignans
23	Caffeic acid	98%	C ₉ H ₈ O ₄	180.0423	
24	Ehyl gallate	98%	C ₉ H ₁₀ O ₅	198.0528	Phenols
25	Gallic acid	98%	C ₇ H ₆ O ₅	170.0215	
26	Vanillic acid	98%	C ₈ H ₈ O ₄	168.0423	

Table S2 Detained information of the drug materials of three TCM species (*Gleditsiae Spina*, GS; *Gleditsiae Sinensis Fructus*, GSF; *Gleditsiae Fructus Abnormalis*, GFA) derived from *Gleditsia sinensis* analyzed in the current work.

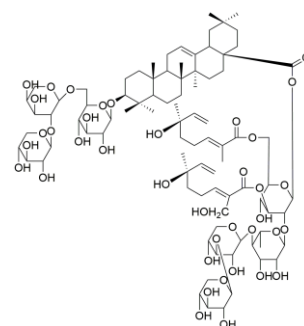
No.	Label	TCM	Producing Regions	Collection Time
1	T-1	GS	Nanyang City, Henan Province	2019.10
2	T-2	GS	Jiujiang City, Jiangxi Province	2019.10
3	T-3	GS	Bijie City, Guizhou Province	2020.04
4	T-4	GS	Chengdu City, Sichuan Province	2020.02
5	T-5	GS	Huixian City, Henan Province	2019.08
6	T-6	GS	Qinling City, Shanxi Province	2019.08
7	T-7	GS	Kunming City, Yunnan Province	2019.08
8	T-8	GS	Neijiang City, Sichuan Province	2019.10
9	T-9	GS	Shiyan City, Hubei Province	2020.04
10	T-10	GS	Luzhou City, Guangxi Province	2019.10
11	T-11	GS	Dezhou City, Shandong Province	2019.10
12	T-12	GS	Bozhou City, Anhui Province	2020.02
13	T-13	GS	Nayong City, Guizhou Province	2020.03
14	T-14	GS	Hechi City, Guangxi Province	2019.12
15	T-15	GS	Tengchong City, Yunnan Province	2019.08
16	F-1	GSF	Bozhou City, Anhui Province	2020.03
17	F-2	GSF	Qufu City, Shandong Province	2019.10
18	F-3	GSF	Jining City, Shandong Province	2019.10
19	F-4	GSF	Baoding City, Hebei Province	2019.06
20	F-5	GSF	Xuzhou City, Jiangsu Province	2020.03
21	F-6	GSF	Taian City, Shandong Province	2019.11
22	F-7	GSF	Yuncheng City, Shanxi Province	2019.12
23	F-8	GSF	Guangan City, Sichuan Province	2020.04
24	F-9	GSF	Nanyang City, Henan Province	2020.03
25	F-10	GSF	Heze City, Shandong Province	2019.10
26	F-11	GSF	Yulin City, Guangxi Province	2019.11
27	F-12	GSF	Luoyang City, Henan Province	2019.10
28	F-13	GSF	Hanzhong City, Shanxi Province	2019.11
29	F-14	GSF	Linyi City, Shandong Province	2019.10
30	F-15	GSF	Nayong City, Guizhou Province	2019.09
31	AF-1	GFA	Jining City, Shandong Province	2019.10
32	AF-2	GFA	Qingchuan City, Sichuan Province	2020.04
33	AF-3	GFA	Zhoucheng City, Shandong Province	2020.02
34	AF-4	GFA	Kunming City, Yunnan Province	2019.08
35	AF-5	GFA	Wannan City, Anhui Province	2019.08
36	AF-6	GFA	Yulin City, Guangxi Province	2019.10
37	AF-7	GFA	Beichuan City, Sichuan Province	2019.09
38	AF-8	GFA	Liuan City, Anhui Province	2019.09

39	AF-9	GFA	Hanzhong City, Shanxi Province	2019.11
40	AF-10	GFA	Baoding City, Heibei Province	2020.03
41	AF-11	GFA	Yaan City, Sichuan Province	2019.10
42	AF-12	GFA	Bozhou City, Anhui Province	2019.10
43	AF-13	GFA	Heze City, Shandong Province	2019.10
44	AF-14	GFA	Xinxiang City, Henan Province	2019.10
45	AF-15	GFA	Guiyang City, Guizhou Province	2019.06

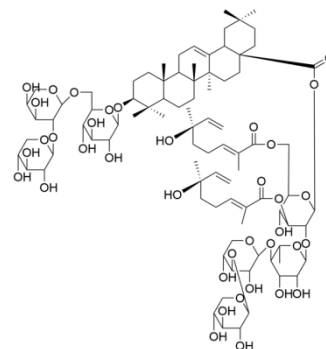
Table S3 In-house library of *Gleditsia sinensis*.

No.	Name	Formula	Accurate molecular mass	Subtype	Chemical Structure
1	Gleditsia saponin C	C ₉₄ H ₁₄₈ O ₄₃	1964.9394		
2	Gleditsioside E	C ₉₄ H ₁₄₈ O ₄₃	1964.9394		
3	Gleditsioside F	C ₉₄ H ₁₄₈ O ₄₂	1948.9445	Triterpenoid saponin	
4	Gleditsioside G	C ₉₄ H ₁₄₈ O ₄₂	1948.9445		
5	Gleditsia saponin B	C ₉₄ H ₁₄₈ O ₄₄	1980.9343		

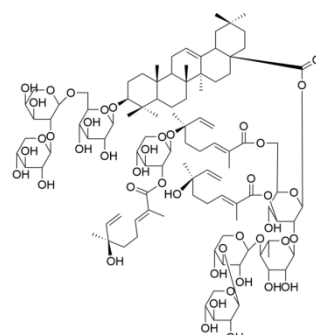
6 Gleditsioside N $C_{88}H_{138}O_{38}$ 1802.8866



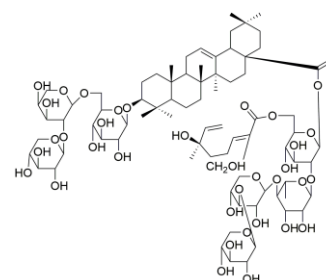
7 Gleditsioside O $C_{88}H_{138}O_{37}$ 1786.8917



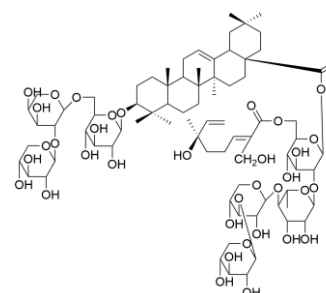
8 Gleditsioside P $C_{103}H_{160}O_{43}$ 2085.0333



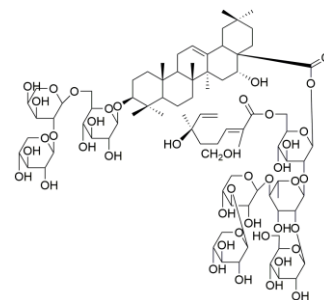
9 Gleditsioside A $C_{78}H_{124}O_{35}$ 1620.7923



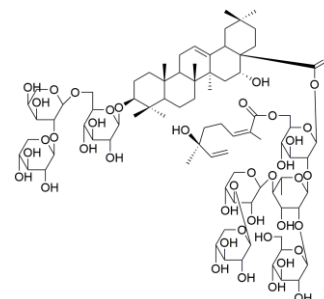
10 Gleditsioside B $C_{78}H_{124}O_{36}$ 1636.7872



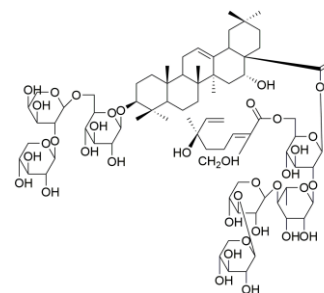
11 Gleditsioside C $C_{84}H_{134}O_{42}$ 1814.8350



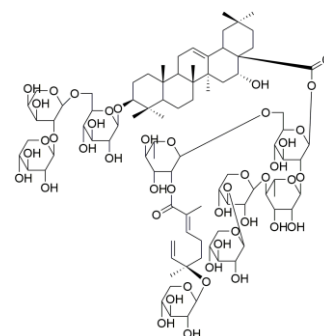
12 Gleditsioside D $C_{84}H_{134}O_{41}$ 1798.8401



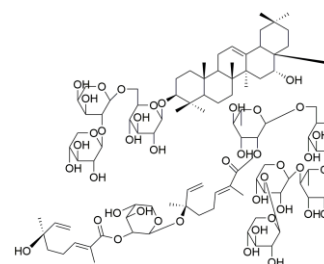
13 Gleditsioside Q $C_{78}H_{124}O_{37}$ 1652.7821



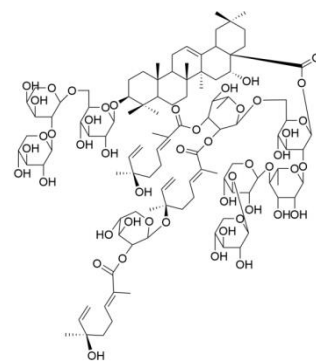
14 Caspicaoside A $C_{89}H_{142}O_{44}$ 1914.8874



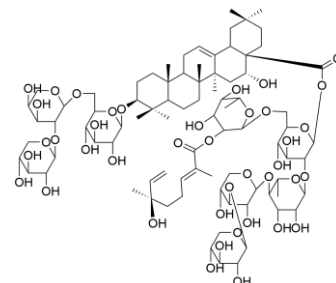
15 Caspicaoside B $C_{99}H_{156}O_{46}$ 2080.9868



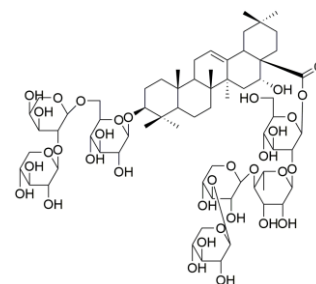
16 Caspicaoside C $C_{109}H_{170}O_{48}$ 2247.0862



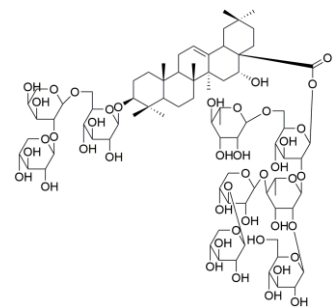
17 Caspicaoside D $C_{84}H_{134}O_{40}$ 1782.8451



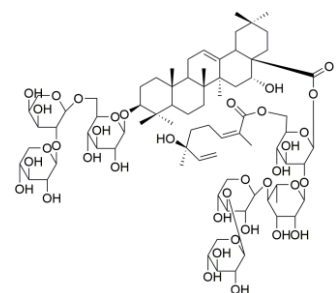
18 Caspicaoside E $C_{68}H_{110}O_{34}$ 1470.6879



19 Caspicaoside F $C_{80}H_{130}O_{43}$ 1778.7986

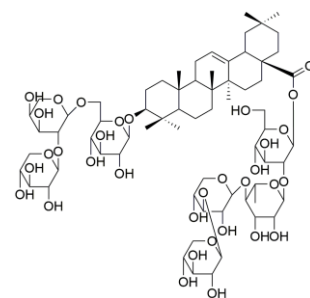


20 Caspicaoside G $C_{78}H_{124}O_{36}$ 1636.7872

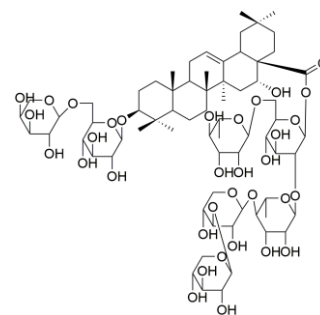


21	Caspicaoside H	$C_{93}H_{146}O_{41}$	1918.9340	
22	Caspicaoside I	$C_{94}H_{148}O_{41}$	1932.9496	
23	Caspicaoside J	$C_{94}H_{148}O_{43}$	1964.9394	
24	Caspicaoside K	$C_{94}H_{148}O_{43}$	1964.9394	
25	Gleditsioside H	$C_{74}H_{120}O_{37}$	1600.7508	

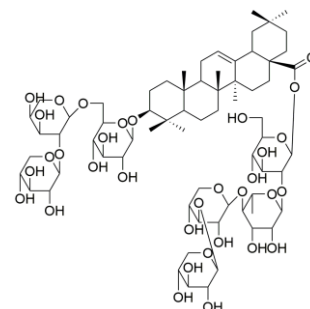
26 Gleditsioside I $C_{68}H_{110}O_{33}$ 1454.6929



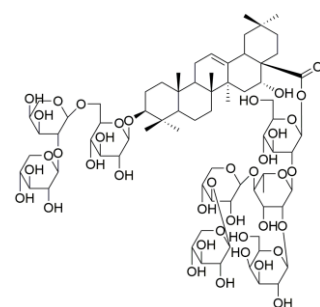
27 Gleditsioside J $C_{69}H_{112}O_{34}$ 1484.7035



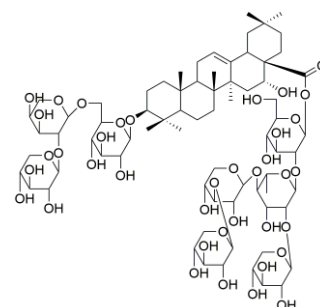
28 Gleditsioside K $C_{68}H_{110}O_{33}$ 1454.6929



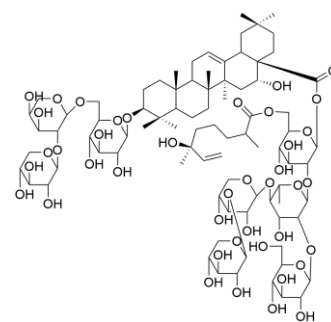
29 Saponin C' $C_{74}H_{120}O_{39}$ 1632.7407



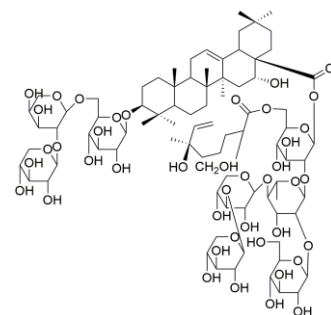
30 Saponin E' $C_{73}H_{118}O_{38}$ 1602.7301



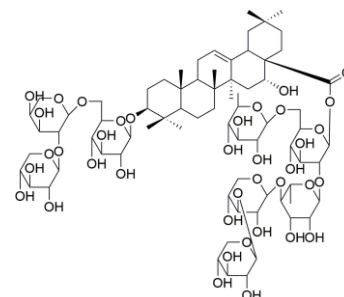
31 Gleditsia saponin J $C_{84}H_{136}O_{41}$ 1800.8557



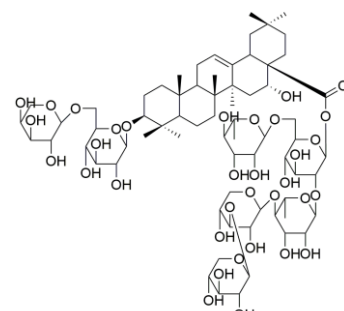
32 Gleditsia saponin K $C_{84}H_{136}O_{42}$ 1816.8506



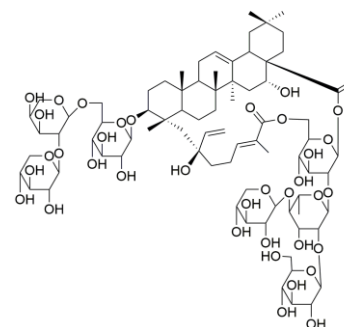
33 Gleditsia saponin C' $C_{74}H_{120}O_{38}$ 1616.7458



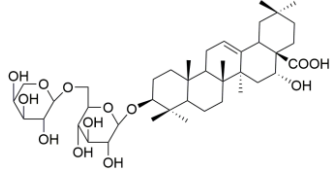
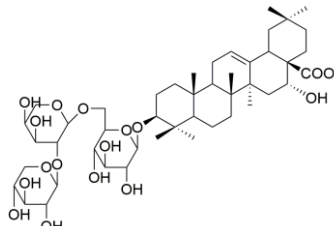
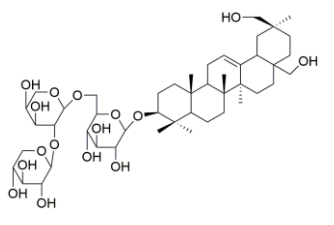
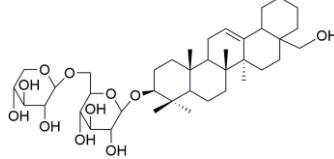
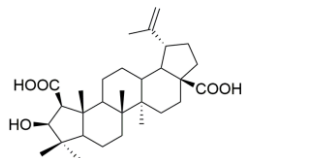
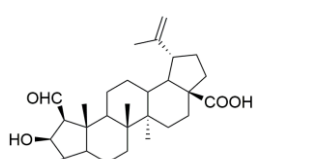
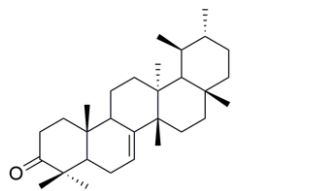
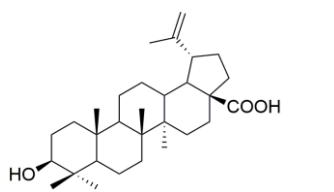
34 Gleditsia saponin E' $C_{69}H_{112}O_{34}$ 1484.7035

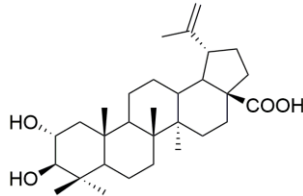
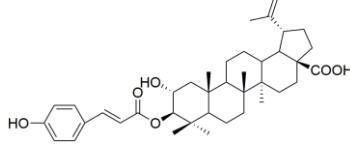
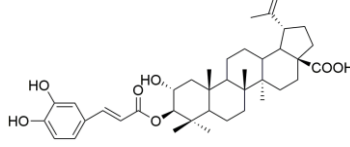
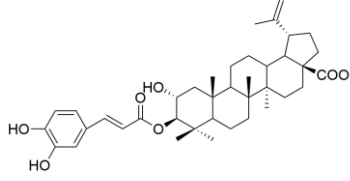
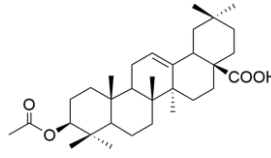
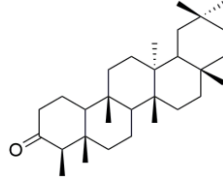
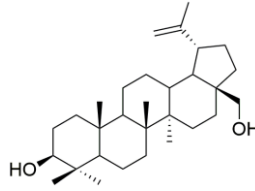
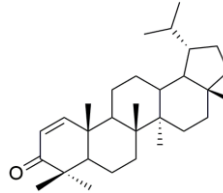


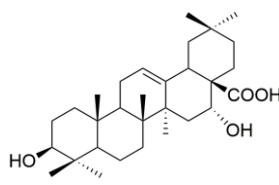
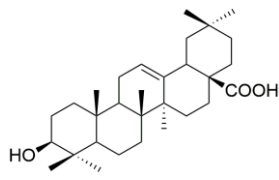
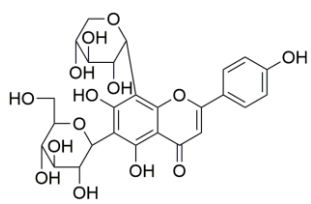
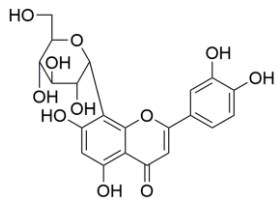
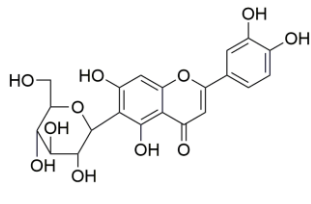
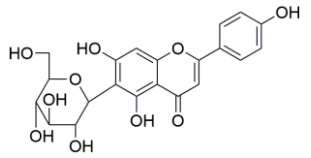
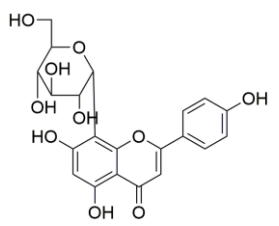
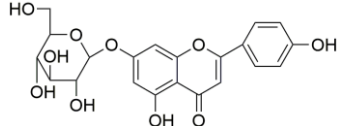
35 Glespinoside A $C_{79}H_{126}O_{37}$ 1666.7978

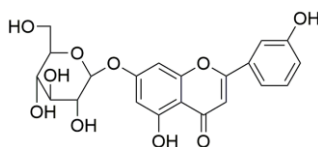
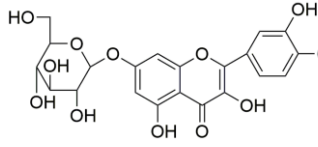
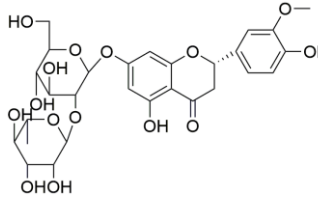
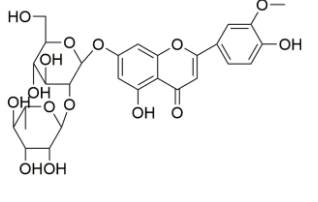
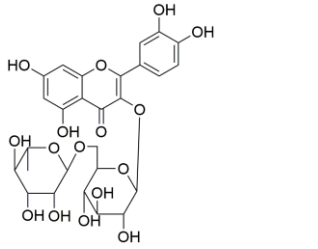
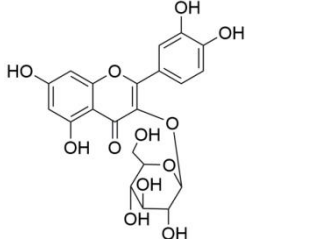
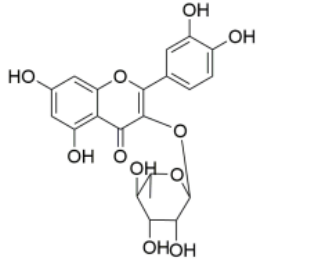


36	<p>3-<i>O</i>-β-D-xylopyranosyl-(1\rightarrow2)-α-L-arabinopyranosyl-(1\rightarrow6)-β-D-glucopyranosyl oleanolic acid 28-<i>O</i>-β-D-xylopyranosyl-(1\rightarrow4)-α-L-rhamnopyranosyl-(1\rightarrow4)-β-D-xylopyranosyl-(1\rightarrow4)-α-L-rhamnopyranosyl-(1\rightarrow3)-β-D-glucopyranosyl ester</p>	C ₇₄ H ₁₂₀ O ₃₇	1600.7508	
37	Gleditsioside Z	C ₆₈ H ₁₀₈ O ₂₇	1356.7078	
38	Caspicaoside L	C ₈₉ H ₁₄₀ O ₃₈	1816.9023	
39	Pitheduloside C	C ₄₆ H ₇₄ O ₁₆	882.4977	
40	Vitalboside A	C ₃₆ H ₅₈ O ₈	618.4132	

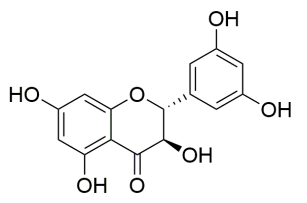
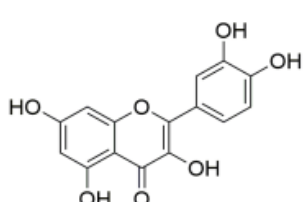
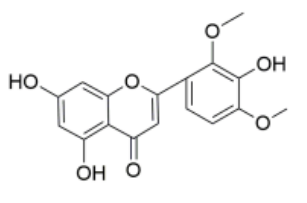
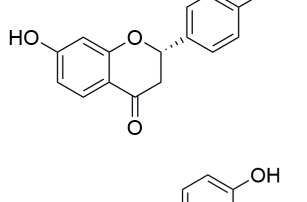
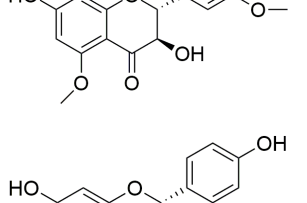
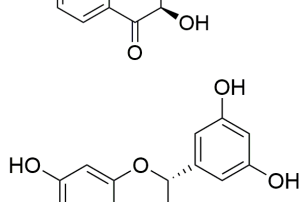
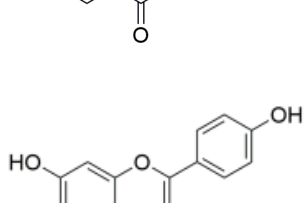
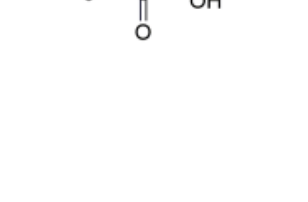
41	Pitheduloside A	C ₄₁ H ₆₆ O ₁₃	766.4503	
42	Pitheduloside E	C ₄₆ H ₇₄ O ₁₇	898.4926	
43	Caspicaoside M	C ₄₆ H ₇₆ O ₁₆	884.5133	
44	Caspicaoside N	C ₄₁ H ₆₈ O ₁₁	736.4762	
<hr/>				
45	2β-carboxyl,3β-hydroxyl-norlupA (1)-20 (29)-en-28-oic acid	C ₃₀ H ₄₆ O ₅	486.3345	
46	Zizyberanalic acid	C ₃₀ H ₄₆ O ₄	470.3396	
Triterpenoid				
47	D-C-friedours-7-en-3-one	C ₃₀ H ₄₈ O	424.3705	
48	Betulic acid	C ₃₀ H ₄₈ O ₃	456.3603	

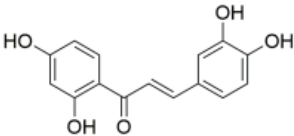
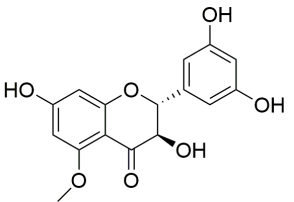
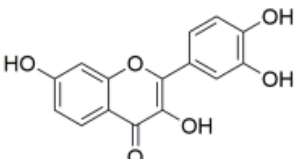
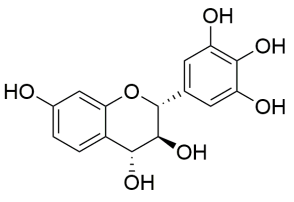
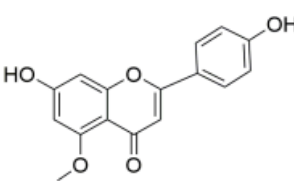
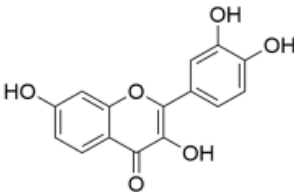
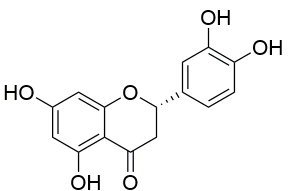
49	Alphitolic acid	C ₃₀ H ₄₈ O ₄	472.3553	
50	3- <i>O</i> - <i>trans</i> - <i>p</i> -coumaroyl alphitolic acid	C ₃₉ H ₅₄ O ₆	618.3920	
51	2-hydroxypyracrenic acid	C ₃₉ H ₅₄ O ₇	634.3870	
52	3β- <i>O</i> - <i>trans</i> - <i>p</i> -caffeoyl alphitolic acid	C ₃₉ H ₅₄ O ₇	634.3870	
53	3β-acetoxyoolean-12-en-28-oic acid	C ₃₂ H ₅₀ O ₄	498.3709	
54	Friedelin	C ₃₀ H ₅₀ O	426.3862	
55	Betulin	C ₃₀ H ₅₀ O ₂	442.3811	
56	Lupenone	C ₃₀ H ₄₈ O	424.3705	

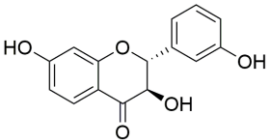
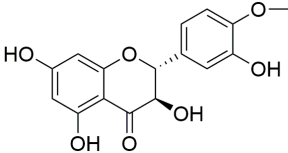
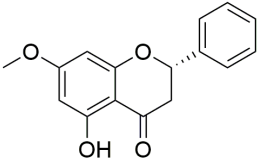
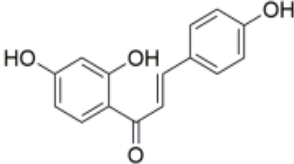
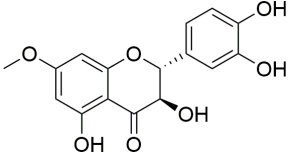
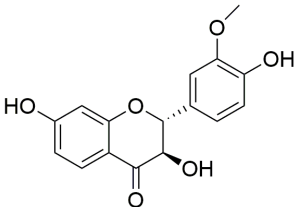
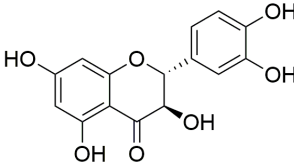
57	Echinocystic acid	$C_{30}H_{48}O_4$	472.3553		
58	Oleanolic acid	$C_{30}H_{48}O_3$	456.3603		
<hr/>					
59	Vicenin-I	$C_{26}H_{28}O_{14}$	564.1479		
60	Orientin	$C_{21}H_{20}O_{11}$	448.1006	Flavonoid C-glycoside	
61	Isorientin	$C_{21}H_{20}O_{11}$	448.1006		
62	Isovitexin	$C_{21}H_{20}O_{10}$	432.1056		
63	5,7,4'-trihydroxyflavone-8-C-glucoside	$C_{21}H_{20}O_{10}$	432.1056		
<hr/>					
64	Luteolin-7-O-beta-galactopyranoside	$C_{21}H_{20}O_{10}$	432.1056	Flavonoid O-glycoside	

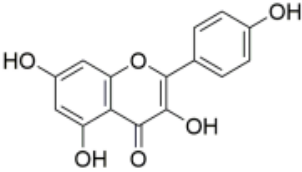
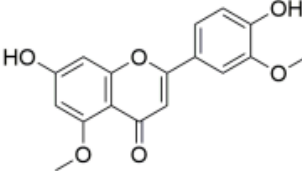
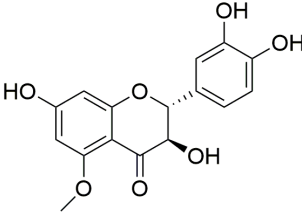
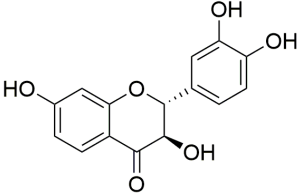
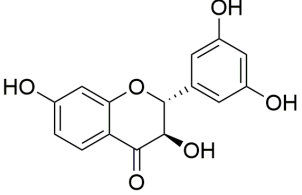
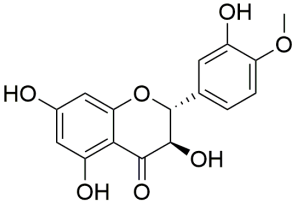
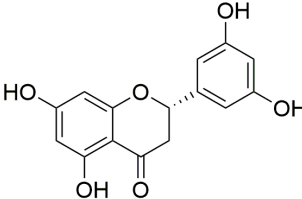
65	Apigenin-7- <i>O</i> - β -glucopyranoside	$C_{21}H_{20}O_{10}$	432.1056	
66	Tamarixin-7- <i>O</i> - β -D-glucoside	$C_{22}H_{22}O_{12}$	478.1111	
67	Neohesperidin	$C_{28}H_{34}O_{15}$	610.1898	
68	Chlorene-7- <i>O</i> -Neohesperidin	$C_{28}H_{32}O_{15}$	608.1741	
69	Rutin	$C_{27}H_{30}O_{16}$	610.1534	
70	Isoquercitrin	$C_{21}H_{20}O_{12}$	464.0955	
71	Quercitrin	$C_{21}H_{20}O_{11}$	448.1006	

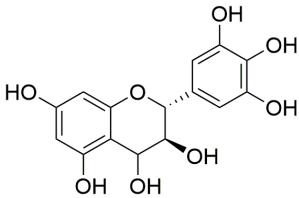
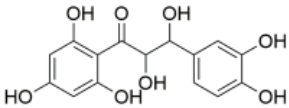
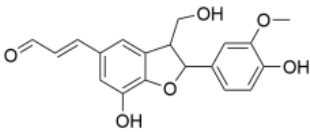
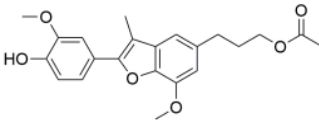
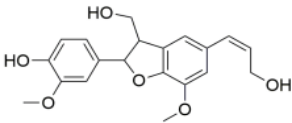
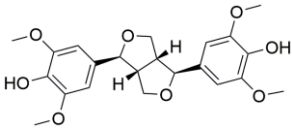
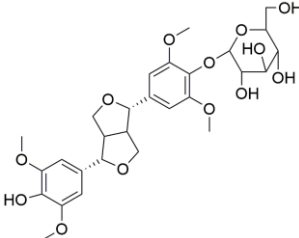
72	Diosmetin-7-O- β -D-glucoside	C ₂₂ H ₂₂ O ₁₁	462.1162		
73	Luteoloside	C ₂₁ H ₂₀ O ₁₁	448.1006		
74	Dihydrokaempferol	C ₁₅ H ₁₂ O ₆	288.0634		
75	Apigenin	C ₁₅ H ₁₀ O ₅	288.0634		
76	Luteolin	C ₁₅ H ₁₀ O ₆	270.0528	Flavonoid	
77	(2R,3R)-5,3',4'-trimethoxy-7-hydroxyl-flavanonol	C ₁₈ H ₁₈ O ₇	346.1053		
78	Epicatechin	C ₁₅ H ₁₄ O ₆	290.0790		

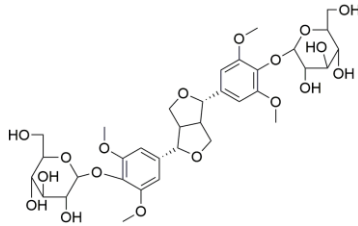
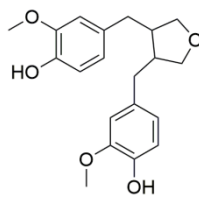
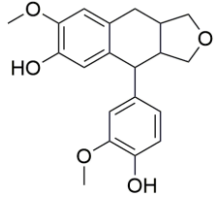
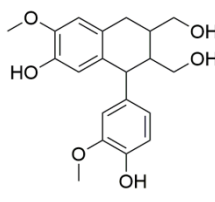
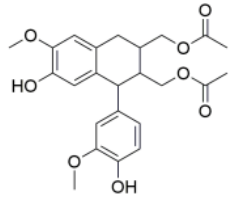
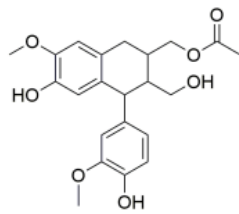
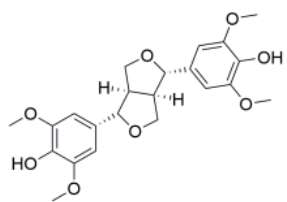
79	5,7,3',5'-tetrahydroxyl-flavanonol	$C_{15}H_{12}O_7$	304.0583	
80	Quercetin	$C_{15}H_{10}O_7$	302.0427	
81	Tricin	$C_{17}H_{14}O_7$	330.0740	
82	Glycyrrhizin	$C_{15}H_{12}O_4$	256.0736	
83	7,4'-dihydroxy-5,3'-dimethoxyflavonol	$C_{17}H_{16}O_7$	332.0896	
84	Chickpamol	$C_{15}H_{12}O_5$	272.0685	
85	7,3',5'-trihydroxydi hydroflavonoids	$C_{15}H_{12}O_5$	272.0685	
86	7,4'-dihydroxyflavonol	$C_{15}H_{10}O_5$	270.0528	

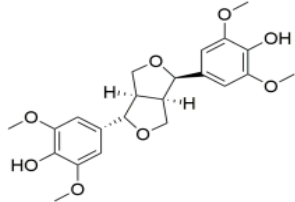
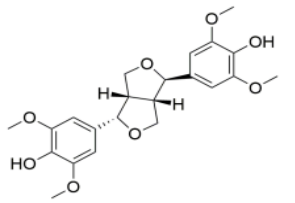
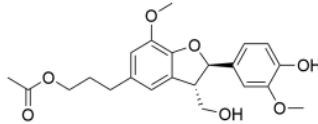
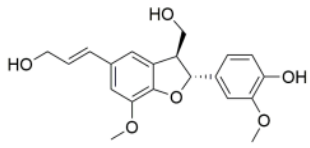
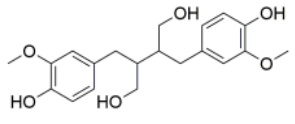
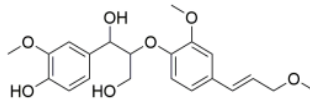
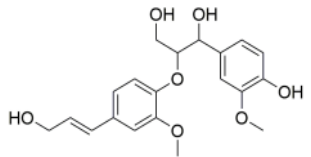
87	Butochalcone	$C_{15}H_{12}O_5$	272.0685	
88	7,3',5'-trihydroxy-5-methoxyflavonol	$C_{16}H_{14}O_7$	318.0740	
89	Fisetin	$C_{15}H_{10}O_6$	286.0477	
90	Leucorobinetinidin	$C_{15}H_{14}O_7$	306.0740	
91	Thevetiaflavone	$C_{16}H_{12}O_5$	284.0685	
92	Fisetin	$C_{15}H_{10}O_6$	286.0477	
93	Eriodictyol	$C_{15}H_{12}O_6$	288.0634	

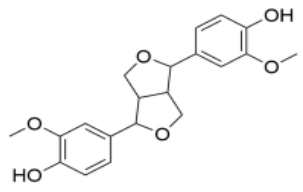
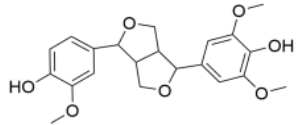
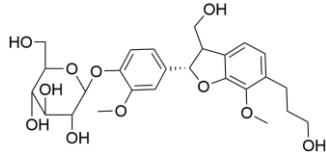
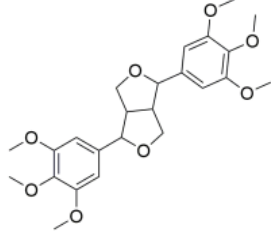
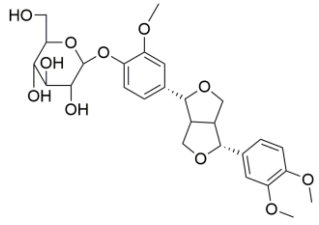
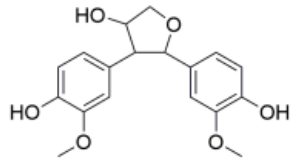
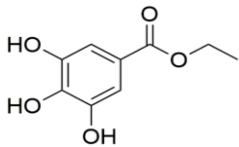
94	Garbanzol	C ₁₅ H ₁₂ O ₅	272.0685	
95	4'- <i>O</i> -methyl-dihydroquercetin	C ₁₆ H ₁₄ O ₇	318.0740	
96	5-hydroxy-7-methoxyflavanone	C ₁₆ H ₁₄ O ₄	270.0892	
97	Isoliquiritigenin	C ₁₅ H ₁₂ O ₄	256.0736	
98	Padmatin	C ₁₆ H ₁₄ O ₇	316.0947	
99	Erycibenin D	C ₁₆ H ₁₄ O ₆	300.0998	
100	Taxifolin	C ₁₅ H ₁₂ O ₇	304.0583	

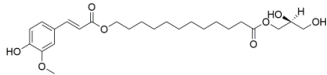
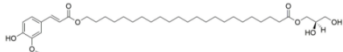

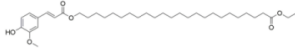
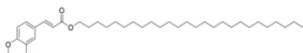
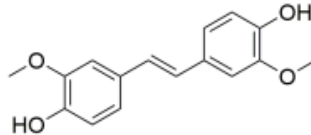
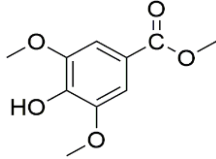
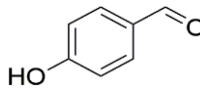
101	Kaempferol	$C_{15}H_{10}O_6$	286.0477	
102	Luteolin-5,3'-dimethyl ether	$C_{17}H_{14}O_6$	314.0790	
103	(2R,3R)-7,3',4'-trihydroxy-5-methoxyflavanonol	$C_{16}H_{14}O_7$	318.0740	
104	Fustin	$C_{15}H_{12}O_6$	288.0634	
105	(2R,3R)-7,3',5'-trihydroxyflavanonol	$C_{15}H_{12}O_6$	288.0634	
106	(2R,3R)-5,7,3'-trihydroxy-4'-methoxyflavanonol	$C_{16}H_{14}O_7$	318.0740	
107	3',5',5,7-Tetrahydroxyflavanone	$C_{15}H_{12}O_6$	288.0634	

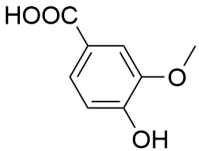
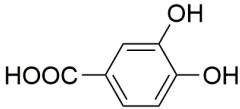
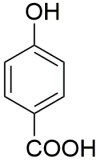
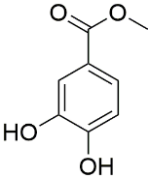
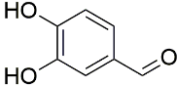
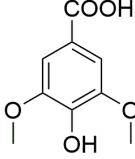
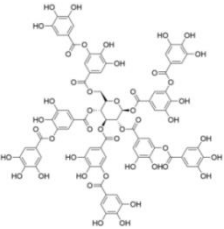
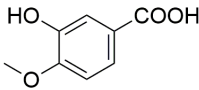
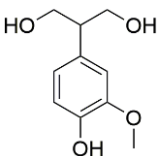
108	Colorless anthocyanins	C ₁₅ H ₁₄ O ₈	322.0689	
109	Cilicicone B	C ₁₅ H ₁₄ O ₈	322.0689	
110	2,3-dihydro-5-(2-formylvinyl)-7-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-benzofuranmethanol	C ₁₉ H ₁₈ O ₆	342.1103	
111	5-(3'-acetoxypropyl)-2-(4'-hydroxy-3'-methoxyphenyl)-7-methoxy-3-methylbenzofuran	C ₂₂ H ₂₄ O ₆	384.1573	
112	Dihydrodehydroiconiferyl alcohol	C ₂₀ H ₂₂ O ₆	358.1416	Lignan 
113	(-)-syringaresinol	C ₂₂ H ₂₆ O ₈	418.1628	
114	Syringaresin-O-β-D-glucopyranoside	C ₂₈ H ₃₆ O ₁₃	580.2156	

115	Liriodendrin	$C_{34}H_{46}O_{18}$	742.2684	
116	(-)-trans-3,4-divanillyltetrahydrofuran	$C_{20}H_{24}O_5$	344.1624	
117	Isoshonanin	$C_{20}H_{22}O_5$	342.1467	
118	(+)-isolariciresinol	$C_{20}H_{24}O_6$	360.1573	
119	Yunnanensin A	$C_{24}H_{28}O_8$	444.1784	
120	Isolariciresinol-9-acetate	$C_{22}H_{26}O_7$	402.1679	
121	(+)-syringaresinol	$C_{22}H_{26}O_8$	418.1628	

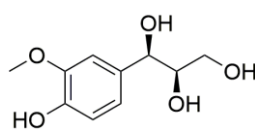
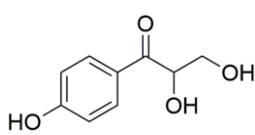
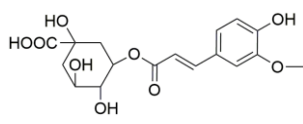
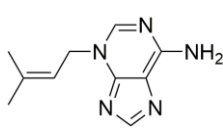
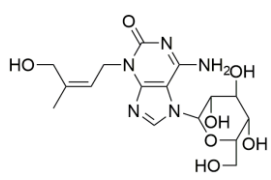
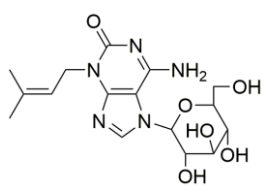
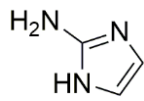
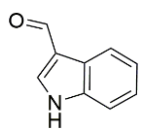
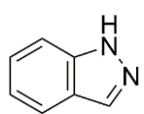
122	(-)-epi-syringaresinol	$C_{22}H_{26}O_8$	418.1628	
123	(+)-epi-syringaresinol	$C_{22}H_{26}O_8$	418.1628	
124	(2R-trans)-2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-(hydroxymethyl)-7-methoxy-5-benzofuranpropanol acetate	$C_{22}H_{26}O_7$	402.1679	
125	(7R,8S)-dehydrodicoumaroyl alcohol	$C_{20}H_{22}O_6$	358.1416	
126	(-)-secoisolariciresinol	$C_{20}H_{26}O_6$	362.1729	
127	Glensin A	$C_{21}H_{26}O_7$	390.1679	
128	Threo-guaiacylglycerol-β-coniferyl aldehyde ether	$C_{20}H_{24}O_7$	376.1522	

129	(+)-pinoresinol	C ₂₀ H ₂₂ O ₆	358.1416		
130	(+)-medioresinol	C ₂₁ H ₂₄ O ₇	388.1522		
131	Dihydrodehydrodic oniferylalcohol-4'- <i>O</i> -β-D-glucoside	C ₂₆ H ₃₄ O ₁₁	522.2101		
132	Epiyangambin	C ₂₄ H ₃₀ O ₈	446.1941		
133	Phillyrin	C ₂₇ H ₃₄ O ₁₁	534.2101		
134	(2R*,3R*,4S*)-2,3- diureido-4-hydroxyt etrahydrofuran	C ₁₈ H ₂₀ O ₆	332.1260		
135	Ethyl gallate	C ₉ H ₁₀ O ₅	198.0528	Phenol	

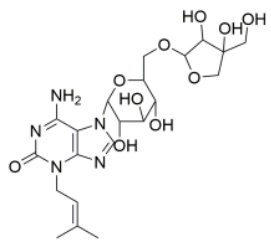
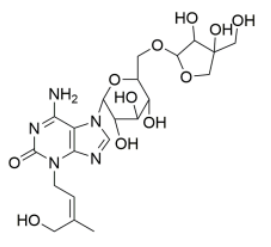
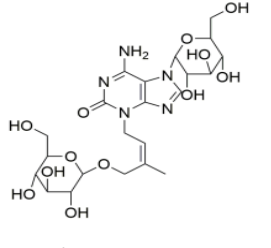
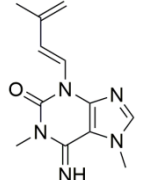
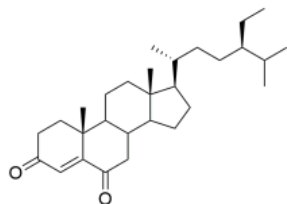
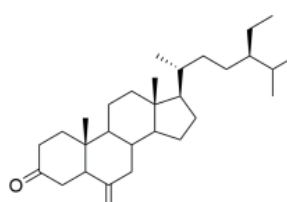
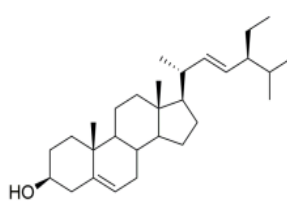
136	2(R)-12-[[[(2E)-3-(4-hydroxy-3-methoxyphenyl)-1-oxo-2-propen-1-yl]oxy]-2,3-dihydroxypropyl ester	$C_{25}H_{38}O_8$	466.2567	
137	2(R)-23-[[[(2E)-3-(4-hydroxy-3-methoxyphenyl)-1-oxo-2-propen-1-yl]oxy]-2,3-dihydroxypropyl ester	$C_{36}H_{60}O_8$	620.4288	
138	2(R)-26-[[[(2E)-3-(4-hydroxy-3-methoxyphenyl)-1-oxo-2-propen-1-yl]oxy]-2,3-dihydroxypropyl ester	$C_{39}H_{66}O_8$	662.4758	
139	Ethyl 24-O-feruloyl-oxytracosanate	$C_{36}H_{60}O_6$	588.4390	
140	N-hexacosanylferulate	$C_{36}H_{62}O_4$	558.4648	
141	(E)-3,3'-dimethoxy-4,4'-dihydroxystilbene	$C_{16}H_{16}O_4$	272.1049	
142	Methyl syringate	$C_{10}H_{12}O_5$	212.0685	
143	p-hydroxyl cinnamaldehyde	$C_9H_8O_2$	148.1384	

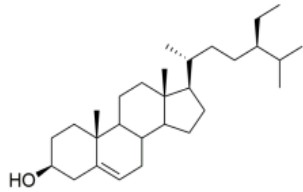
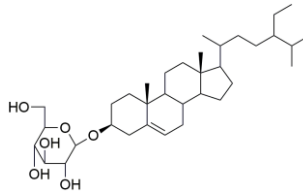
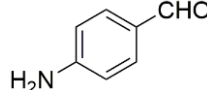
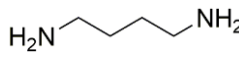
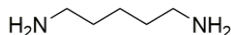
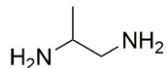
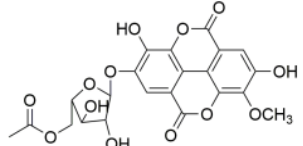
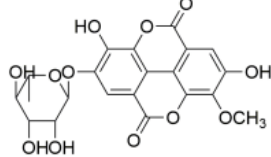
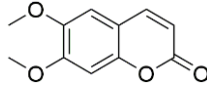
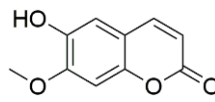
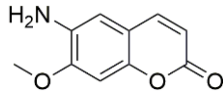
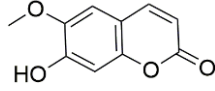
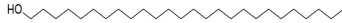
144	Vanillic acid	$C_8H_8O_4$	168.0423	
145	Protocatechuic acid	$C_7H_6O_4$	154.0266	
146	p-hydroxybenzoic acid	$C_7H_6O_3$	138.0317	
147	Methyl Protocatechin	$C_8H_8O_4$	168.0423	
148	Protocatechualdehyde	$C_7H_6O_3$	138.0317	
149	Syringic acid	$C_9H_{10}O_5$	198.0528	
150	Tannin	$C_{76}H_{52}O_{46}$	1700.1730	
151	Isovanillic acid	$C_8H_8O_4$	168.0423	
152	2-guaiacylpropane-1,3-diol	$C_{10}H_{14}O_4$	198.0892	

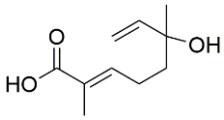

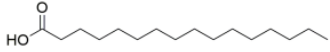
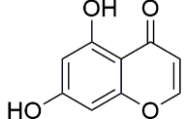
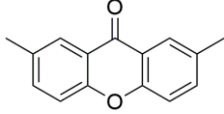
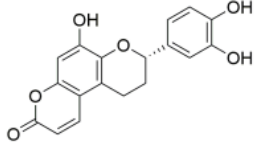
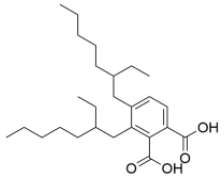
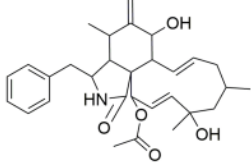
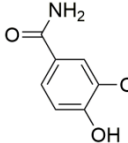

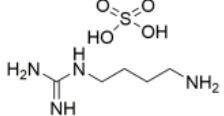
153	Caffeic acid	C ₉ H ₈ O ₄	180.0423		
154	Trans-coniferyl aldehyde	C ₁₀ H ₁₀ O ₃	178.0630		
155	Sinapaldehyde	C ₁₁ H ₁₂ O ₄	208.0736		
156	Cinnamic acid	C ₉ H ₈ O ₂	148.0524		
157	Trans-caffeic acid	C ₉ H ₈ O ₄	180.0423	Phenylpropanoid	
158	3,4'-dihydroxypropionophenone	C ₉ H ₁₀ O ₃	166.0630		
159	Dihydroferulic acid	C ₁₀ H ₁₂ O ₄	196.0736		
160	C-veratroyl glycol	C ₁₀ H ₁₂ O ₅	212.0685		
161	4-[6-O-(4-hydroxy-3,5-dimethoxybenzoyl)-β-D-glucopyranosyloxy]-ferulic acid	C ₂₅ H ₂₈ O ₁₃	536.1530		

162	(-)-(7R,8R)-threo-guaiacylglycerol	C ₁₀ H ₁₄ O ₅	214.0841	
163	Walnut D	C ₉ H ₁₀ O ₄	182.0579	
164	3-O-trans-ferulylquinic acid	C ₁₇ H ₂₀ O ₉	368.1107	
165	Triacanthin	C ₁₀ H ₁₃ N ₅	203.1171	
166	Saikachinoside A	C ₁₆ H ₂₃ N ₅ O ₇	397.1597	
167	Locustoside A	C ₁₆ H ₂₃ N ₅ O ₆	381.1648	
168	2-aminoimidazole	C ₃ H ₅ N ₃	83.0483	
169	Indole-3-carbaldehyde	C ₉ H ₇ NO	145.0528	
170	Indazole	C ₇ H ₆ N ₂	118.0531	

Alkaloid

171	Locustoside B	$C_{21}H_{31}N_5O_{10}$	513.2071		
172	Saikachinoside B	$C_{21}H_{31}N_5O_{11}$	529.2020		
173	Saikachinoside C	$C_{22}H_{33}N_5O_{12}$	559.2126		
174	Dioicine	$C_{12}H_{15}N_5O$	245.1277		
<hr/>					
175	Stigmast-4-ene-3,6-dione	$C_{29}H_{46}O_2$	426.3498		
176	Stigmast-3,6-dione	$C_{29}H_{48}O_2$	428.3654	Sterol	
177	Stigmasterol	$C_{29}H_{48}O$	412.3705		

178	β -sitosterol	C ₂₉ H ₅₀ O	414.3862		
179	Daucosterol	C ₃₅ H ₆₀ O ₆	576.4390		
180	4-aminoben-zaldehy de	C ₇ H ₇ NO	121.0528		
181	Putrescine	C ₄ H ₁₂ N ₂	88.1000	Amine	
182	Cadaverine	C ₅ H ₁₄ N ₂	102.1157		
183	Diaminopropane	C ₃ H ₁₀ N ₂	74.0844		
184	3-O-methylellagic acid-4'-(5''-acetyl)- α -L-arabinofuranosi de	C ₂₂ H ₁₈ O ₁₃	490.0747		
185	3-O-methylellagic acid-4'-O- α -L-rham nopyranoside	C ₂₁ H ₁₈ O ₁₂	462.0798		
186	Scoparone	C ₁₁ H ₁₀ O ₄	206.0579		
187	Isoscopoletin	C ₁₀ H ₈ O ₄	192.0423	Coumarin	
188	6-amino-7-methoxy coumarin	C ₁₀ H ₉ NO ₃	191.0582		
189	Scopoletin	C ₁₀ H ₈ O ₄	192.0423		
190	Cerylalcohol	C ₂₆ H ₅₄ O	382.4175	Other	

191	Monoterpenic acid	$C_{10}H_{16}O_3$	184.1099	
192	Octacosanoic acid	$C_{28}H_{56}O_2$	424.4280	
193	Palmitic acid	$C_{16}H_{32}O_2$	256.2402	
194	5,7-dihydroxychromone	$C_9H_6O_4$	178.0266	
195	2,7-dimethyl-xanthone	$C_{15}H_{12}O_2$	224.0837	
196	(2S)-2-(3',4'-dihydroxyphenyl)-3,4-tetrahydro-8-hydroxy-2H,8H-benzo[1,2-b:3,4-b']dipyran-2-one	$C_{18}H_{14}O_6$	326.0790	
197	Bis(2-ethylheptyl)ortho-phthalate	$C_{26}H_{42}O_4$	418.3083	
198	Cytochalasin H	$C_{30}H_{39}NO_5$	493.2828	
199	4-hydroxy-3-methoxybenzamide	$C_8H_9NO_3$	167.0582	
200	Nonacosane	$C_{29}H_{60}$	408.4695	
201	Agmatine	$C_5H_{16}N_4O_4S$	228.0892	

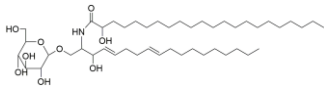
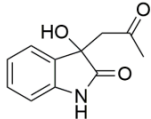
202	1- <i>O</i> - β -D-glucopyranosyl-(2 <i>S</i> , 3 <i>R</i> , 4 <i>E</i> , 8 <i>E</i>)-2-[(2-hydroxyhexadecanoyl)amido]-4,8-octadecadiene-1, 3-diol	$C_{46}H_{87}NO_9$	797.6381	
203	3-(2-oxopropyl)-3-hydroxy-indolin-2-one	$C_{11}H_{11}NO_3$	205.0739	

Table S4 Detailed information of the potential differential components identified by comparing the chemical fingerprinting information of three TCM species derived from *Gleditsia sinensis*.

No.	VIP	t _R (min)	Observed m/z	Precursors/Add uct/Isotope	Mass error (ppm)	Formula	identical	ESI-MS ² fragments (POS)	ESI-MS ² fragments (NEG)	GFA	GSF	GS
M1	22.61	30.45	1003.2476	[M+H] ⁺	0.84	C ₃₁ H ₅₄ O ₃₆	C ₁₃ H ₂₆ O ₂₀ -2Glc-GluA	1003.2466,827.7066,665.496 8,503.1079,445.1202,429.08 92,371.1017,355.0705,281.0 517	/	/	/	/
M2 ^a	18.47	2.14	398.1675	[M+H] ⁺	1.24	C ₁₆ H ₂₃ N ₅ O ₇	Saikachinoside A ^a	398.1673,380.1564,353.1345 ,314.1101,282.1339,218.103 9,203.9710,152.0570,135.03 02	396.1517,315.0722,234.0994, 218.1039,167.0350,131.0347	/	/	/
M3	17.83	16.83	1965.9491	[M+H] ⁺	1.22	C ₉₄ H ₁₄₈ O ₄₃	Caspicaoside J/Caspicaoside K/Gleditsia saponin C/Gleditsioside E or its isomer (EA-2Glc-2Rha-4Xyl-2Ter-O H)	1965.9487,1833.9066,1701.8 638,1569.8206,1423.7630,12 91.7215,1129.6681,1067.455 6,935.4136,803.3706,771.34 44,609.2916,477.2491,459.2 385,455.3527,295.1544	1964.9353,1946.9255,1934.9 246,1782.8400,1764.8296,15 98.7300,1579.7166,1451.673 9,1349.6382,1331.6275,1217. 5949,1063.5829,939.4961,89 7.4852,879.4745,765.4425,71 7.2453,469.1558,451.1450,36 7.1239,281.0878,263.0771	C	C	/

	10.17	16.82	1965.4405	[2M+H] ²⁺	/	/	/	1966.9525,1834.9100,1701.8638,1569.8206,1423.7630,1291.7215,1199.4975,1129.6681,1067.4556,1049.4452,935.4136,917.4034,771.3444,639.3014,753.3336,609.2916,587.2852,477.2491,459.2385,455.3527,295.1544	1964.9353,1946.9255,1934.9246,1763.8257,1597.7271,1579.7166,1349.6382,1331.6275,1217.5949,1063.5829,939.4961,897.4852,879.4745,717.2453,635.2540,469.1558,281.0878,145.0506,131.0350			
M4	16.72	19.00	1949.9533	[M+H] ⁺	0.76	C ₉₄ H ₁₄₈ O ₄₂	Gleditsioside F or its isomer (EA-2Glc-2Rha-4Xyl-2Ter)	1949.9532,1817.9105,1685.8674,1553.8247,1535.8453,1407.7676,1345.5549,1183.5018,1165.4916,1051.4604,1033.4492,919.4182,901.4073,887.3914,755.3489,479.2646,461.2539,443.2434,295.1544	1993.9431,1947.9370,1763.8263,1597.7269,1349.6380,1331.6277,1217.5950,939.4957,897.4852,879.4746,765.4427,635.2550,571.1869,535.1678,469.1558,337.1137,281.0878,183.1026,131.0351	C	C	/
	8.38	18.99	1949.4432	[2M+H] ²⁺	/	/	/	1950.9567,1818.9140,1817.9105,1685.8674,1553.8247,1535.8153,1407.7680,1183.5018,1165.4916,1051.4604,1033.4492,919.4182,901.4073,755.3489,625.3216,593.2960,479.2646,461.2539,443.2434,295.1544	1994.9469,1948.9409,1763.8263,1597.7269,1349.6380,1331.6277,1217.5950,939.4957,897.4852,879.4746,635.2550,469.1558,409.1344,337.1137,323.0983,281.0878,183.1026,131.0351			

M5	15.57	12.83	1981.9438	[M+H] ⁺	1.08	C ₉₄ H ₁₄₈ O ₄₄	Gleditsia saponin B or its isomer (EA-2Glc-2Rha-4Xyl-2(Ter-OH))	1981.9439,1849.9012,1717.8583,1571.8006,1440.7624,1439.7585,1307.7165,1145.6632,1083.4505,951.4082,933.3976,787.3398,769.3288,637.2864,607.261,493.2439,475.2334,455.3528,411.1500,339.1082,311.1501,295.1029,293.1388,265.0924,259.0815,229.0711,211.0603,201.1634,165.0908,163.0606	1980.9294,1962.9189,1943.9048,1932.9083,1761.8104,1749.8106,1649.6800,1597.7261,1469.6800,1349.6376,1289.6152,1199.5848,1061.5678,1049.5667,981.5045,939.4956,897.4849,879.4744,747.4317,633.2392,571.3995,469.1557,451.1453,409.1347,281.0877,181.0869,143.0351	C	C	/
	8.18	12.84	1982.4413	[2M+H] ²⁺	/	/	/	1982.9475,1850.9042,1717.8583,1571.8006,1439.7585,1145.6632,1083.4505,933.3976,787.3398,637.2864,475.2334,455.3528,437.3419,427.1448,311.1501,295.1029,211.0603,163.0606	1980.9294,1962.9189,1944.9086,1943.9048,1932.9083,1761.8104,1749.8106,1579.7167,1469.6800,1349.6376,1289.6152,1199.5848,1061.5678,1049.5667,981.5045,939.4956,897.4849,879.4744,747.4317,633.2392,571.3995,469.1557,451.1453,409.1347,281.0877,181.0869,143.0351			

M6	14.92	19.89	1949.9533	[M+H] ⁺	0.76	C ₉₄ H ₁₄₈ O ₄₂	Gleditsioside G or its isomer (OA-2Glc-2Rha-4Xyl-2Ter-OH)	1949.9530,1817.9112,1685.8 682,1553.8251,1407.7676,13 31.5401,1199.4976,1067.455 4,935.4134,753.3336,609.29 10,495.2597,477.2491,459.2 384,295.1546	1930.9316,1918.9311,1765.8 420,1748.8357,1582.7362,13 33.6434,1315.6330,881.4906, 749.4478,617.4053,455.3526	C	C	/
M7	14.35	5.06	514.2149	[M+H] ⁺	1.08	C ₂₁ H ₃₁ N ₅ O ₁₀	Locustoside B	514.2150,446.1522,435.1283 ,314.1098,220.1190,152.057 0,137.0598	512.1994,449.1653,387.1437, 357.0993,315.1461,218.1047, 150.0324,149.0247,133.0143	/	/	/
M8	14.28	30.77	439.3573	[M+H] ⁺	1.75	C ₃₀ H ₄₆ O ₂	2-Methyl-7-(2-methyl-2-propa nyl)-2-[(3E,7E)-4,8,12-trimeth yl-3,7,11-tridecatrien-1-yl]-6-c hromanol or its isomer	439.3575,421.3459,395.3143 ,381.3149,349.2895,327.268 4,273.2212,233.1899,191.17 94,141.9834,139.9881,135.1 167,121.1011	/	/	/	C
M9	12.77	14.44	1799.8479	[M+H] ⁺	0.29	C ₈₄ H ₁₃₄ O ₄₁	Gleditsioside D or its isomer (EA-3Glc-Rha-4Xyl-Ter)	1799.8481,1667.8057,1535.7 627,1517.7513,1385.7092,13 55.6989,1223.6558,1077.598 0,1033.3970,901.3553,751.3 020,637.2719,455.3522,311. 1493	1797.8324,1631.7333,1613.7 217,1533.7472,1511.6900,14 81.6808,1469.6818,1367.652 0,897.4853,765.4421,715.229 6,631.2086,571.1873,281.087 8,131.0351	C	C	/

M10	12.65	17.24	1833.9064	[M+H] ⁺	0.31	C ₈₉ H ₁₄₀ O ₃₉	EA-2Glc-2Rha-3Xyl-2Ter-OH	1833.9068,1569.8201,1361.5499,1199.4972,1129.6679,1067.4549,935.4135,917.4024,771.3439,623.3049,591.2790,495.2597,477.2491,459.2380,455.526,299.1492,277.1437	1831.8904,1814.8843,1802.8834,1650.7988,1632.7884,1466.6939,1200.5893,765.4433,469.1562,451.1454,337.1140	C	C	/
M11	12.52	15.90	1965.9469	[M+H] ⁺	0.11	C ₉₄ H ₁₄₈ O ₄₃	Caspicaoside J/Caspicaoside K/Gleditsia saponin C/Gleditsioside E or its isomer (EA-2Glc-2Rha-4Xyl-2Ter-OH)	1965.9467,1833.9036,1815.8924,1701.8607,1683.8506,1569.8190,1551.8080,1405.7511,1067.4539,935.4114,917.4014,785.3582,753.3320,591.2797,587.2845,477.2487,459.2381,455.3524,293.1385	1964.9334,1946.9230,1934.9230,1782.8384,1764.8276,1761.8083,1598.7293,1579.7153,1332.6291,1290.6183,1063.5817,897.4844,633.2150,469.1554,451.1450,337.1136,281.0876,263.0770,145.0506,131.0350	C	C	/
M12	12.36	10.16	1601.7593	[M+H] ⁺	0.74	C ₇₄ H ₁₂₀ O ₃₇	Gleditsioside H or its isomer (OA-2Glc-2Rha-4Xyl)	1601.7598,1469.7173,1337.6752,1175.6210,1029.5636,897.5218,751.4632,719.2616,573.2033,441.1608,439.3575,279.1078	1599.7440,1467.7012,1333.6437,1201.6011,1069.5588,923.5014,881.4908,717.2457,455.3527,263.0774	C	C	/

M13	12.11	16.61	1637.7963	[M+H] ⁺	1.11	C ₇₈ H ₁₂₄ O ₃₆	Gleditsioside B or its isomer (OA-2Glc-Rha-4Xyl-Ter-OH)	1637.7962,1505.7538,1373.7 117,1355.7004,1223.6574,10 77.6003,887.3414,755.2987, 605.2453,459.1879,439.3580 ,327.1444,299.1497,281.138 8	1618.7704,1605.7675,1454.6 879,1436.6776,1304.6349,12 02.6026,923.5019,881.4895,7 49.4470,571.1870,469.1554,1 31.0351	C	C	/
M14	12.03	13.98	1783.8533	[M+H] ⁺	0.49	C ₈₄ H ₁₃₄ O ₄₀	Caspicaoside D or its isomer (OA-4Xyl-2Rha-2Glc-Ter-OH)	1784.8566,1783.8532,1651.8 106,1519.7682,1387.7257,12 41.6675,901.3558,769.3130, 605.2442,473.2021,439.3575 ,311.1495	1781.8354,1764.8294,1582.7 352,1450.6933,1318.6481,12 01.5998,923.5008,881.4899,7 49.4472,617.4048,469.1556,4 55.3525,263.0773,181.0869	C	C	/
M15	12.02	19.79	1621.7995	[M+H] ⁺	-0.04	C ₇₈ H ₁₂₄ O ₃₅	Gleditsioside A or its isomer (OA-4Xyl-2Rha-2Glc-Ter)	1621.7996,1489.7575,1339.7 042,1207.6620,1061.6041,73 9.3019,721.2912,589.2495,4 43.1916,439.3575,311.1495	1619.7850,1453.6858,1435.6 753,1333.6430,1303.6323,12 01.6004,1069.5583,923.5008, 881.4904,749.4476,571.1874, 469.1557,409.1345,263.0773	C	C	/
M16	11.83	17.16	1965.9480	[M+H] ⁺	0.64	C ₉₄ H ₁₄₈ O ₄₃	Caspicaoside J/Caspicaoside K/Gleditsia saponin C/Gleditsioside E or its isomer (EA-2Glc-2Rha-2Ter-OH-4Xyl)	1965.9480,1701.8631,1555.8 055,1423.7624,1291.7198,11 29.4466,1083.4501,933.3978 ,801.3546,655.2968,493.243 6,475.2333,313.1654,163.06 02	1946.9272,1928.9170,1916.9 163,1904.9166,1765.8428,17 46.8217,1581.7345,1563.724 1,1449.6913,1317.6439,1185. 5977,923.5024,881.4911,749. 4484,617.4057,455.3530,181. 0872	C	C	/

M17	11.25	10.79	1617.7551	[M+H] ⁺	1.26	C ₇₄ H ₁₂₀ O ₃₈	Gleditsia saponin C' or its isomer (EA-2Glc-2Rha-4Xyl)	1617.7559,1485.7136,1323.6599,1191.6172,1059.5753,867.2999,735.2570,603.2143,573.2041,441.1616,309.1198,279.1080	1615.7360,1483.6933,1453.6828,1351.6481,1333.6392,1201.5989,1085.5510,923.5000,881.4887,749.4462,631.2080,455.3519,277.0926	/	/	/
M18	11.02	10.86	1915.8963	[M+H] ⁺	0.85	C ₈₉ H ₁₄₂ O ₄₄	Caspicaoside A or its isomer (EA-2Glc-2Rha-5Xyl-Ter)	1915.8966,1783.8534,1651.8107,1519.7675,1339.6884,1281.4870,1149.4443,1017.4019,885.3599,753.3163,607.2597,577.2496,455.3525,445.2074,427.1967,313.1653,295.1544	1914.8820,1795.8140,1783.8163,1651.7790,1597.7258,1469.6791,1383.6939,1349.6369,1217.5938,1015.3862,939.4949,897.4845,765.4419,717.2445,633.3994,571.3990,469.1554,337.1135	C	C	/
M19	11.01	9.41	1763.8124	[M+H] ⁺	0.82	C ₈₀ H ₁₃₀ O ₄₂	OA-3Glc-2Rha-4Xyl	1763.8125,1631.7694,1499.7264,1337.6733,1191.6165,1013.3570,881.3148,719.2612,573.2033,271.0969,151.0393	1761.7963,1629.7273,1497.7082,1335.6561,1189.6018,1025.5324,881.4900,879.2986,749.4473,617.4051,455.3526,367.1242	/	/	/
M20	10.89	30.55	457.3681	[M+H] ⁺	0.94	C ₃₀ H ₄₈ O ₃	Isomer of oleanolic acid	457.3678,445.1204,411.3619,383.3297,349.2697,301.2163,245.2260,243.2109,191.1792,175.1478,137.1324	455.3515	C	C	C

M21 ^a	10.88	5.97	305.0661	[M+H] ⁺	1.79	C ₁₅ H ₁₂ O ₇	taxifolin ^a	305.0660,289.0697,259.0606 ,231.0658,195.0291,167.034 2,153.0184,149.0235,123.04 42,121.0283	303.0509,285.0403,259.0610, 241.0499,217.0506,177.0191, 151.0037,125.0244,123.0450	C	C	C
M22	10.70	16.96	1637.7971	[M+H] ⁺	1.60	C ₇₈ H ₁₂₄ O ₃₆	Gleditsioside B or its isomer (OA-2Glc-Rha-4Xyl-Ter-OH)	1637.7972,1505.7553,1373.7 128,1241.6694,1095.6107,88 7.3420,755.2987,623.2562,4 91.2134,473.2027,439.3579, 327.1447,165.0912	1635.7806,1618.7732,1606.7 696,1454.6899,1436.6798,13 04.6367,1172.5932,923.5014, 881.4909,749.4478,617.4055, 571.1877,469.1561,409.1348, 337.1139	C	C	/
M23	10.60	11.41	1653.7906	[M+H] ⁺	0.68	C ₇₈ H ₁₂₄ O ₃₇	Gleditsioside Q or its isomer (EA-2Glc-Rha-4Xyl-Ter-OH)	1653.7904,1521.7477,1389.7 060,1239.6522,1093.5945,10 31.3818,961.5526,799.4994, 755.2970,623.2551,473.2020 ,455.3524,327.1438,309.131 9	1651.7751,1634.7672,1622.7 672,1470.6845,1452.6738,13 31.6276,1319.6275,1187.585 1,1025.5328,1007.5210,981.5 065,963.4961,951.4994,939.4 961,897.4858,879.4750,765.4 429,633.2386,571.1875,469.1 559,337.1140	C	C	/
M24 ^a	10.45	5.71	433.1133	[M+H] ⁺	0.94	C ₂₁ H ₂₀ O ₁₀	Vitexin ^a	433.1132,415.1025,397.0920 ,337.0711,313.0714,283.060 8,271.0601,229.0859,153.01 82	431.0980,383.0773,341.0665, 311.0563,283.0611,269.0452, 239.0694,151.0396,124.0116 4	C	C	C

M25	10.43	12.14	1455.7017	[M+H] ⁺	1.04	C ₆₈ H ₁₁₀ O ₃₃	Gleditsioside I or its isomer (OA-2Glc-Rha-4Xyl)	1455.7018,1323.6595,1191.6170,1161.6059,1029.5638,897.5219,751.4634,573.2035,441.1610,439.3577,427.1454,295.1030,279.1078	1453.6858,1321.6434,1201.6005,1069.5584,923.5009,881.4903,749.4477,571.1876,469.1559,439.1453,337.1138,263.0772,131.0351	C	C	/
M26	10.20	10.71	1815.8434	[M+H] ⁺	0.66	C ₈₄ H ₁₃₄ O ₄₂	Gleditsioside Cor its isomer (EA-3Glc-4Xyl-Rha-Ter-OH)	1815.8438,1683.8011,1551.7582,1389.7056,1257.6628,1243.6479,1111.6052,1093.5949,1049.3925,917.3513,767.2973,635.2552,455.3526,295.1029,265.0923,163.0605	1813.8253,1796.8185,1784.8180,1632.7340,1614.7235,1531.7298,1481.6776,1451.6667,1217.5938,939.4957,897.4842,765.4418,571.1869,469.1552,367.1237,281.0874,131.0350	C	C	/
M27 ^a	9.89	4.56	382.1724	[M+H] ⁺	0.69	C ₁₆ H ₂₃ N ₅ O ₆	Locustoside A ^a	382.1723,345.1526,314.1099,249.1123,152.0570,135.0302	380.1570,287.0558,218.1043,179.0561,150.0420	/	/	/
M28	9.74	17.73	1753.8423	[M+H] ⁺	0.33	C ₈₃ H ₁₃₂ O ₃₉	OA-2Glc-Rha-Ter-Xyl	1753.8421,1621.7987,1489.7557,1357.7126,1225.6750,1093.6361,1079.6160,1063.4292,983.6089,871.3453,739.3029,607.2603,491.2273,439.3568,295.1024,265.0919	1751.8255,1619.7783,1453.6846,1435.6743,1333.6416,1321.6420,1189.5976,1069.5588,881.4896,749.4473,617.4051,455.3521,263.0771,181.0870	C	C	/

M29	9.57	31.50	647.4615	[M+H] ⁺	-0.85	C ₃₁ H ₆₆ O ₁₃	C ₂₅ H ₅₈ O ₇ -GluA	629.4760,578.6592,510.4628 ,479.3351,425.3775,384.194 0,365.2667,312.3241,307.18 77	/	C	C	C
M30	9.38	14.69	1799.8495	[M+H] ⁺	1.21	C ₈₄ H ₁₃₄ O ₄₁	Gleditsioside D or its isomer (OA-4Xyl-Rha-3Glc-Ter-OH)	1799.8493,1667.8070,1535.7 636,1373.7113,1211.4519,10 49.3941,917.3518,785.3089, 653.2661,491.2134,473.2026 ,439.3578,427.1447,327.144 5,295.1030,279.1075	1797.8324,1780.8054,1768.8 253,1616.7380,1598.7306,14 65.6854,1453.6852,1333.643 3,1153.5785,881.4902,749.44 69,617.4052,469.1558,455.35 27,367.1240,263.0774,181.08 71	/	/	/
M31	9.37	12.94	1783.8545	[M+H] ⁺	1.18	C ₈₄ H ₁₃₄ O ₄₀	Caspicaoside D or its isomer (EA-4Xyl-2Rha-2Glc-Ter)	1783.8542,1651.8110,1519.7 692,1387.7261,1207.6570,11 79.4563,1047.4152,885.3614 ,753.3190,459.2236,445.207 8,313.1653,295.1545	1781.8364,1649.7922,1615.7 371,1597.7270,1465.6836,13 49.6377,1217.5951,1199.584 2,1063.5824,939.4957,897.48 51,717.2451,469.1558,451.14 52,337.1136	C	C	/

M32	9.30	14.83	1899.7498	[M+H] ⁺	0.30	C ₈₉ H ₁₄₂ O ₄₃	OA-2Glc-2Rha-Ter-5Xyl	1899.9012,1767.8581,1635.8 149,1503.7719,1357.7137,12 81.4870,1149.4447,1017.402 1,978.4155,885.3600,753.31 74,607.2597,445.2073,439.3 576,313.1652,295.1542,265. 0917	1898.8879,1751.8165,1749.8 113,1737.8096,1599.7415,15 67.7161,1435.6731,1333.642 3,1315.6319,1201.5998,1069. 5588,881.4901,749.4471,617. 4047,469.1558,455.3521,315. 1447,263.0774	C	C	/
M33	9.17	10.38	1798.8402	[M+H] ⁺	0.10	C ₈₄ H ₁₃₄ O ₄₁	Gleditsioside D or its isomer (EA-3Glc-3Xyl-Rha-Ara-Ter)	1799.8475,1667.8045,1535.7 627,1403.7202,12576620,10 77.5982,901.3552,769.3119, 587.2287,455.3522,311.1494	1797.8317,1780.8250,1768.8 247,1616.7409,1598.7304,14 66.6884,1349.6381,1319.631 9,1217.5947,1085.5535,939.4 956,897.4856,879.4746,717.2 452,633.2387,469.1557,451.1 452,409.1346,337.1137,281.0 878,263.0773,131.0351	C	C	/
M34	9.14	28.70	441.3729	[M+H] ⁺	0.01	C ₃₀ H ₄₈ O ₂	Isomer of betulinaldehyde	441.3726,423.3623,411.3622 ,203.1796,177.1638,163.148 1,149.1326,133.1012,121.10 13	/	C	C	C
M35	9.09	30.90	663.4548	[M+H] ⁺	3.38	C ₃₁ H ₆₆ O ₁₄	C ₂₄ H ₅₃ O ₈ -CH ₃ -Rha	647.4621,628.3751,482.1507 ,413.3771,341.1988	/	C	C	C

M36	8.70	8.70	1617.7547	[M+H] ⁺	1.02	C ₇₄ H ₁₂₀ O ₃₈	Gleditsia saponin C' or its isomer (EA-2Glc-2Rha-4Xyl)	1617.7544,1485.7126,1353.6704,1221.6273,1191.6163,1059.5743,1045.5590,927.5321,913.5173,719.2614,573.2032,455.3526,441.1610,437.3419,279.1076	1615.7377,1483.6951,1349.6379,1217.5949,1085.5529,981.5056,897.4851,879.4743,765.4421.717.2451,585.2034,469.1557,337.1138,263.0772,131.0351	C	C	/
M37	8.70	7.05	357.1340	[M+H] ⁺	1.42	C ₁₆ H ₂₁ O ₉	C ₁₀ H ₁₁ O ₄ -Glc	357.1338,327.1232,307.0965,179.0707,161.0599,137.0599	355.1191,313.1071,187.0974,125.0971	C	C	C
M38	8.66	16.50	1833.7598	[M+H] ⁺	0.31	C ₈₉ H ₁₄₀ O ₃₉	EA-2Glc-2Rha-Ter-(Ter-OH)-3Xyl	1833.9046,1701.8603,1569.8188,1405.7494,1275.7220,1199.4944,1067.4535,935.4133,917.3985,771.3425,676.4420,623.3094,609.2906,573.2025,495.2589,477.2486,311.1490,295.1546	1831.8758,1814.8798,1802.8746,1650.7955,1632.7842,1465.6979,1199.5887,939.5077,897.4845,879.4740,747.4507,	C	C	/

M39	8.66	13.68	1783.8528	[M+H] ⁺	0.19	C ₈₄ H ₁₃₄ O ₄₀	Caspicaoside D or its isomer (OA-2Glc-2Rha-4Xyl-Ter-OH)	1783.8528,1651.8100,1519.7 677,1387.7251,1241.6669,11 65.4391,1033.3974,901.3555 ,769.3128,637.2707,605.244 1,439.3572,311.1495,295.10 28	1781.8348,1763.8259,1751.8 257,1599.7417,1581.7319,14 49.6892,1333.6425,1315.631 8,1201.5998,923.5005,881.49 00,749.4468,617.4050,599.39 45,455.3524,409.1349,307.10 35,263.0773,215.0561,163.06 17,127.0403	C	C	/
M40	8.29	9.93	1642.7844	[M+H] ⁺	0.003	C ₇₆ H ₁₂₃ O ₃₇ N	C ₃₁ H ₄₆ O ₂ N-3Glc-3Xyl-2Rha	1642.7846,1510.7422,1378.7 000,1232.6411,1086.5835,92 4.5319,792.4886,660.4466,4 68.1716,336.1293,204.0869	1640.7705,1508.7279,1374.6 704,1242.6273,1110.5848,96 4.5267,922.5172,790.4741,71 7.2455,658.4323,469.1559,45 5.3526,409.1345,307.1036	C	C	/
M41	8.22	8.50	1779.8069	[M+H] ⁺	0.57	C ₈₀ H ₁₃₀ O ₄₃	Caspicaoside F or its isomer(EA-3Glc-2Rha-4Xyl)	1779.8067,1647.7642,1485.7 109,1353.6690,1207.6104,11 45.3975,1013.3564,881.3146 ,719.2606,573.2029,471.170 8,455.3522,441.1606,309.11 86,279.1078	1777.7905,1631.7299,1615.7 370,1513.7026,1349.6362,12 03.5862,1041.5254,897.4847, 879.2985,765.4419,631.2086, 571.1872,469.1553,409.1350, 367.1240	C	/	/
M42	8.12	32.24	707.1696	[M+H] ⁺	0.84	C ₂₈ H ₃₄ O ₂₁	C ₁₁ H ₁₀ O ₄ -3CHO-3COOH-Xyl- Rha	707.1692,441.2981,429.0891 ,371.1013,355.0703,341.018 5,281.0514,266.9998,223.06 40,207.0325,147.0655	/	C	C	C

M43	8.08	31.31	338.3427	[M+H] ⁺	0.01	C ₂₂ H ₄₃ ON	16-Amino-1-cyclohexylidene-1-hexadecanol or its isomer	338.3427,321.3158,303.3052,282.2791,254.2481,240.2327,226.2167,191.1795,177.1639,163.1483,149.1327,135.1170.121.1014	/	C	C	C
	10.25	31.30	675.6766	[2M+H] ⁺	/	/	/	675.6762,629.4745,578.4813,523.4272,487.3478,441.3325,394.2591,376.3189,360.3239,338.3427,321.3158,303.3052,296.3315,163.1483,149.1327,135.1170.121.1014	/			
M44	8.06	9.06	1633.7497	[M+H] ⁺	1.07	C ₇₄ H ₁₂₀ O ₃₉	Gleditsioside J or its isomer (EA-3Glc-Rha-4Xyl)	1633.7493,1501.7071,1339.6542,1207.6117,1075.5688,913.5165,867.2992,735.2562,573.2035,455.3523,441.1607,295.1028	1631.7336,1499.6904,1469.6805,1349.6360,1205.5960,1043.5431,897.4854,765.4425,733.2403,631.2087,571.1873,469.1558,443.1401,409.1343,281.0878,263.0771	C	C	/

M45	8.02	16.00	2126.9923	[M+H] ⁺	3.38	C ₁₀₀ H ₁₅₈ O ₄₈	EA-2Glc-3Rha-2(Ter-OH)-4Xyl	2127.9996,1995.9557,1863.9135,1731.8704,1585.7038,1555.8044,1423.7619,1291.7186,11129.6668,1083.4624,933.3962,771.3433,639.3008,477.2488,455.3524,295.1028,265.0921	2125.9819,2108.9754,2096.9750,1944.8911,1926.8803,1794.8363,1632.7379,1512.6929,1371.6971,1209.4792,1045.3952,1043.3815,1027.3859,879.4733,765.4415,631.2080,499.1657,367.1238,263.0769	C	C	/
M46	9.81	30.96	803.5439	[M+H] ⁺	0.68	C ₅₀ H ₇₄ O ₈	(3β)-Lup-20(29)-ene-3,28-diyl (1S,4R,1'S,4'R)bis(4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate) or its isomer	803.5441,783.5749,767.5959,731.4747,681.3630,665.0634,615.4465,593.1356,565.1409,513.3519,479.3374,4227.3564	/	C	C	C
	15.98	30.95	413.2668	In-source fragmentation	/	/	/	413.2669,393.2981,149.0237	/			
	9.30	30.97	393.2980	In-source fragmentation	/	/	/	393.2980,301.1414,167.034,149.0236,121.0285	/			

Table S5 The NMR data of compounds Saikachinoside A (DMSO-*d*₆ at 500 MHz) and Locustoside A (CD₃OD:D₂O=1:9 at 600 MHz).

No.	Saikachinoside A		Locustoside A	
	δ_C , type	δ_H (J in Hz)	δ_C , type	δ_H (J in Hz)
2	154.9, C		158.1, C	
4	153.0, C		153.9, C	
5	102.6, C		104.8, C	
6	153.5, C		154.9, C	
8	142.9, CH	8.09, s	145.2, CH	8.14, s
1'		4.59, d (7.1)	42.8, CH ₂	4.57, m
2'	121.0, CH	5.26, brt (6.8)	118.8, CH	5.14, brt
3'	139.4, C		139.2, C	
4'	59.9, CH ₂	4.11, brs	25.9, CH ₃	1.68, brs
5'	21.3, CH ₃	1.68, s	18.6, CH ₃	1.77, brs
1''	86.4, CH	5.42, d (8.5)	88.1, CH	5.60, d (5.64)
2''	72.5, CH	3.33, m	73.5, CH	3.70, m
3''	76.3, CH		76.7, CH	3.70, m
4''	68.0, CH	3.46, m	69.2, CH	3.77, dd (9.69, 2.90)
5''	79.3, CH	3.51, dt (9.5, 2.2t)	80.1, CH	3.80, m
6''	58.9, CH	3.66	60.1, CH ₂	3.96, d (12.5) 3.91, d (12.6)