Electronic Supplementary Material (ESI) for Analytical Methods

Characterization of phenolic constituents in *Lithocarpus polystachyus*

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Figure S1: UHPLC-PAD/ESI-MS^n analysis of the leaves of *L. polystachyus*: (a) UHPLC-PAD chromatography; (b) ESI-MS total ion current (TIC) profile of *L. polystachyus*; and (c) ESI-MS extract ion current (EIC) of some trace constituents

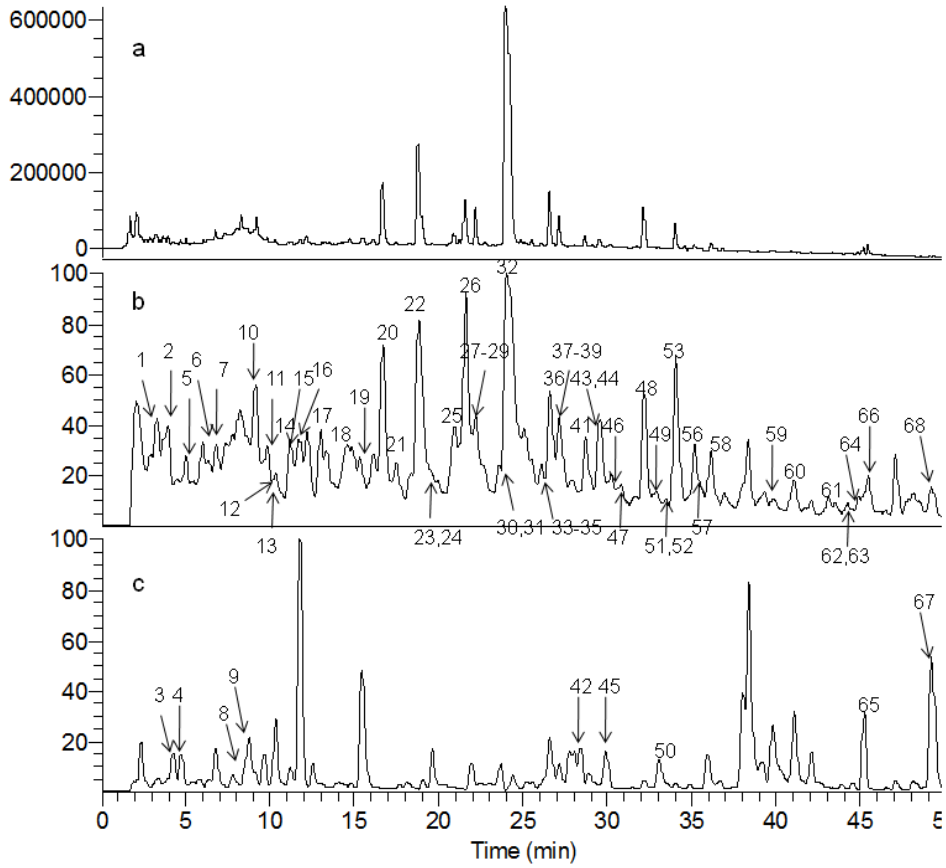

Figure S2: UPLC-PAD/ESI-MS analysis of the mixture of 16 standards. (a) UPLC-PAD chromatography; (b) ESI-MS total ion current (TIC)

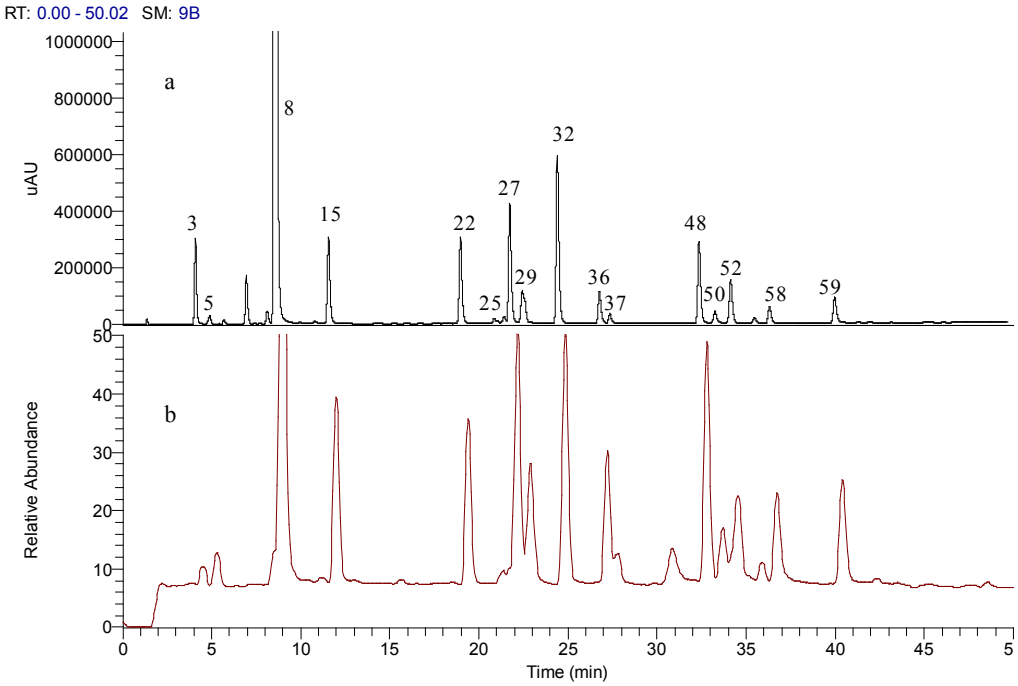

Figure S3: MS/MS product ion mass spectra of Luteolin-4'-*O*-rhamnosyl (1→2) glycoside (**18**, *m/z* 593)

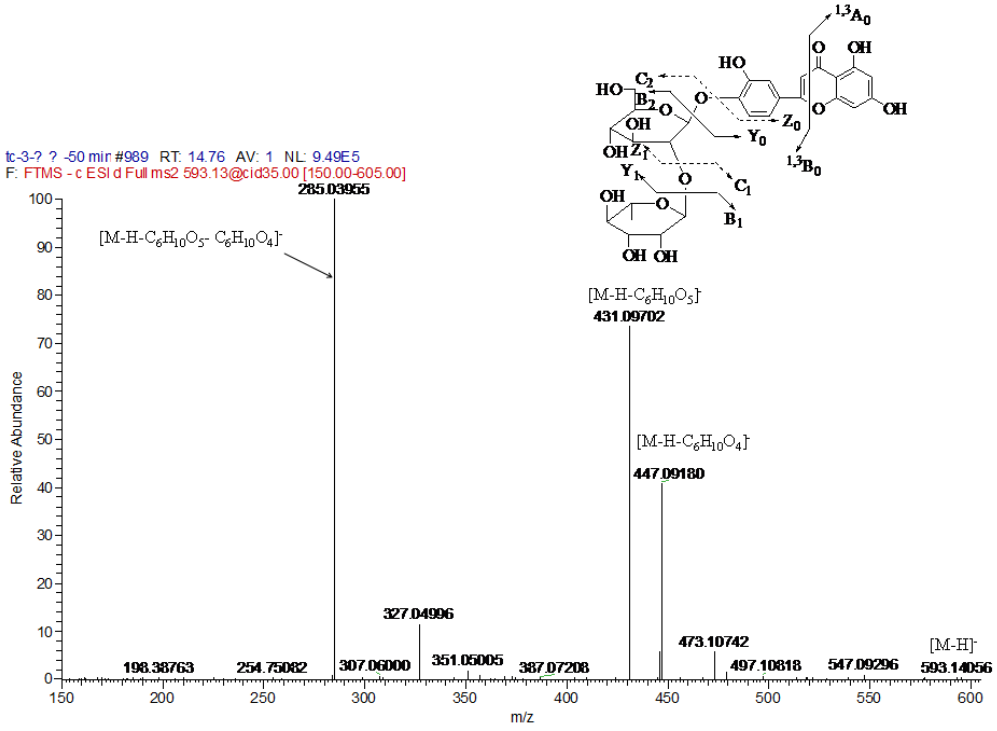

Figure S4: MS/MS product ion mass spectra of phlorizin -di-*O*-glucoside (**20**, *m/z* 597)

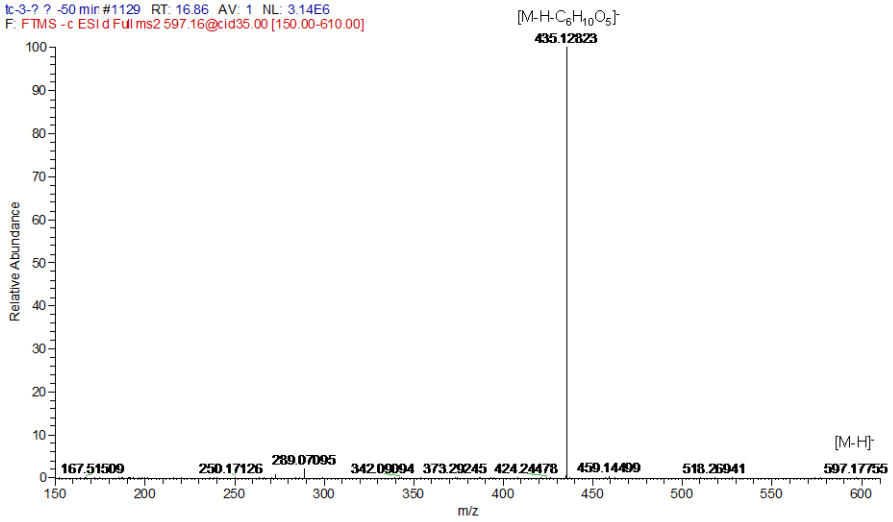

Figure S5: MS/MS product ion mass spectra of phloretin2-O-[β-D-apiofuranosyl(1→6)-β-D-glucopyranoside (**27**, *m/z* 567)

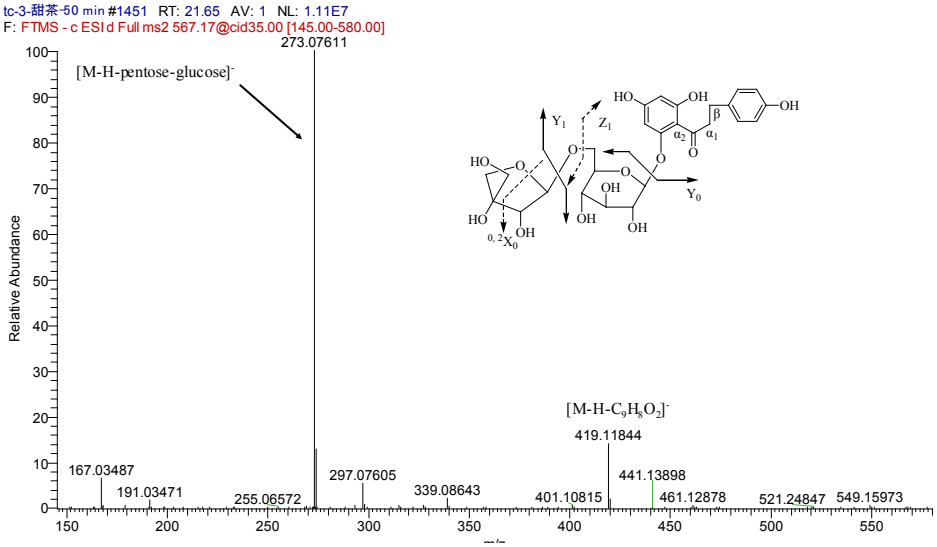

Figure S6: MS/MS product ion mass spectra of phloretin-2-*O*-coumaroyl- glucoside (**61**, *m/z* 581)

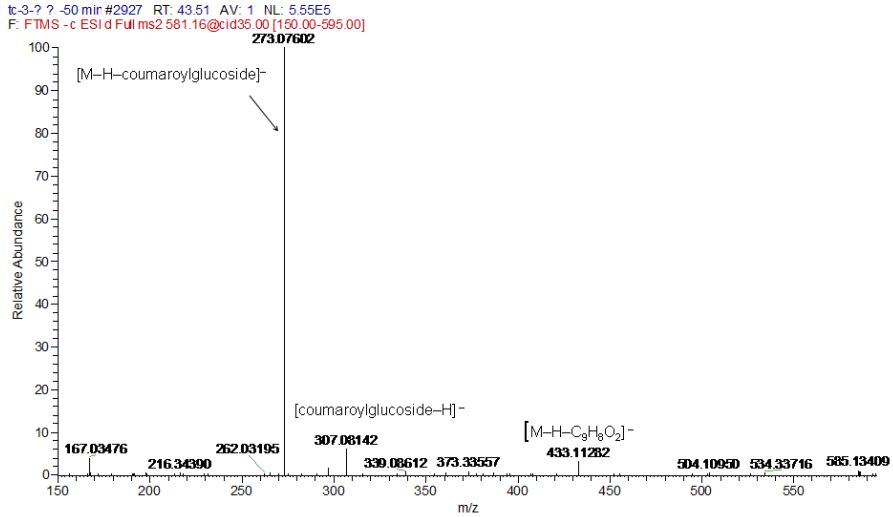

Table S1. Characterization of phenolic constituents of *L. polystachyus* by UHPLC-PAD/ESI-MS^n

No.	t_R (min)	Observed Mass	Calculated Mass	Error (ppm)	Formula	LC/MS^n data (% base peak)	Identification
1[b]	3.2	315.07224	315.07216	-2.1	$C_{13}H_{15}O_9$	MS^2[315]153.01921(100) MS^3[315→153]109.0(100)	Protocatechuic acid hexoside
2[b]	3.9	447.11359	447.11441	0.5	$C_{18}H_{23}O_{13}$	MS^2[447]315.07114(100),271.08151 (59); MS^3[447→315] 153.0(100)	Dihydroxybenzoic acid hexoside pentoside
3[a b]	4.2	153.01936	153.01933	2.8	$C_7H_5O_4$	MS^2[153]109.02959 (100)	Protocatechuic acid
4[b]	4.7	371.09760	371.09837	0.5	$C_{16}H_{19}O_{10}$	MS^2[371]325.09177(43), 163.03984(100); MS^3[325→163] 119.1(100)	phenolic acid hexoside
5[a b]	5.0	289.07126	289.07176	-1.7	$C_{15}H_{13}O_6$	MS^2[289]245.08128(100), 205.05022(37),179.03470(14)	Catechin
6[b]	6.7	341.08704	341.08781	-2.2	$C_{15}H_{17}O_9$	MS^2[341]179.03464(100), 135.04509(8)	Caffeic acid hexoside
7[b]	6.8	325.09225	325.09289	1.0	$C_{15}H_{17}O_8$	MS^2[341]163.03986(100), 119.05030(12)	*p*-comaroylhexoside
8[a b]	8.5	179.03481	179.03498	2.3	$C_9H_7O_4$	MS^2[179] 135.04506(100)	Caffeoyl acid
9[b]	8.8	449.10822	449.10894	-2.1	$C_{21}H_{21}O_{11}$	MS^2[449]287.05515(100), 269.04 468 (30), 259.06042 (33);MS^2[449→287] 269.1(5), 259.1(100), 243.2 (15)	flavanonol-7-*O*-hexoside 1
10[b]	8.9	341.08701	341.08781	-2.4	$C_{15}H_{17}O_9$	MS^2[341] 179.03464(100);MS^3[341→179] 135.0(100)	Caffeoyl hexoside
11[b]	9.6	449.10803	449.10894	-2.0	$C_{21}H_{21}O_{11}$	MS^2[449]287.05524(33), 269.04474 (100), 259.06049(40); MS^3[449→287] 269.1(6), 259.1(100), 243.2(18)	flavanonol-7-*O*-hexoside 2
12[b]	10.2	337.09210	337.09289	-2.4	$C_{16}H_{17}O_8$	MS^2[337]191.05571(100), 173.04530 (7), 163.03986 (6)	5-*p*-coumaroylquinic acid
13[b]	10.3	449.10782	449.10894	0.5	$C_{21}H_{21}O_{11}$	MS^2[449]287.05511(100); MS^3[449→287] 151.1(100)	Eriodictyol hexoside 1
14[b]	11.1	609.14478	609.14611	-2.4	$C_{27}H_{29}O_{16}$	MS^2 [609] 489.10178(10), 463. 08676 (50), 462.07883 (25), 447.09186 (100), 301.03442(33), 285.03958(10) MS^3[609→447]327.2(17), 300.1(32), 284.1(100), 255.1(18), 150.9(4)	Quercetin7-*O*-hexoside-3-*O*-rhamnoside
15[a b]	11.4	335.07660	335.07669	-2.0	$C_{16}H_{15}O_8$	MS^2[335]179.03470(100), 135.04515(23)	5-*O*-caffeoylshikimic acid
16[b]	11.8	449.10818	449.10894	0.6	$C_{21}H_{21}O_{11}$	MS^2[449] 287.05521(100); MS^3[449→287] 151.0(100)	Eriodictyol hexoside 2
17[b]	13.5	163.04002	163.04007	-0.4	$C_9H_7O_3$	MS^2[163] 119.05023(100)	Coumaric acid
18[b]	14.8	593.14966	593.15119	-2.3	$C_{27}H_{29}O_{15}$	MS^2[593]473.10751(6), 447.09186 (41), 431.09708(71), 327.04996(11),	Luteolin-4'-*O*-rhamnosyl(1→2)glycoside

						285.03958(100); MS^3[593→285]: 267.1(40), 257.0 (19), 255.2(24), 243.0 (76), 239.1 (47), 229.2 (100), 213.2 (69), 211.1 (24),199.1 (29), 187.1 (25), 185.1 (33), 169.1(37), 163.1 (17), 151.1 (23)	
19 [b]	15.4	449.10904	449.10894	0.2	$C_{21}H_{21}O_{11}$	MS^2[449]287.05557(100); MS^3[449→287] 151.0(100)	Eriodictyol hexoside 3
20 [b]	16.9	597.18256	597.18249	0.1	$C_{27}H_{33}O_{15}$	MS^2[597]:435.12888 (100); MS^3[597→435]: 273.0(100), 167.0(26)	Phlorizin -di-*O*-glucoside
21 [b]	18.3	597.18280	597.18249	0.5	$C_{27}H_{33}O_{15}$	MS^2[597] 449.12857(5), 297.07590 (2), 273.07648 (100); MS^3[597→273] 167.1(100)	Phloretin-2-*O*-glucosyl (1→6) glucoside
22 [a]	18.8	451.12439	451.12459	-0.1	$C_{21}H_{23}O_{11}$	MS^2[451]289.07126(100); MS^3[451→289]271.2(100), 245.2(18), 167.1(95),125.0(43)	3-Hydroxyphlorizin
23 [b]	19.1	447.09238	447.09329	-2.0	$C_{21}H_{19}O_{11}$	MS^2[447]327.05011(10), 285.03964(100); MS^3[447→285]267(14), 257(19), 243(24), 241(100), 217(31), 213(23), 201(11), 199(40), 175(32), 151(19)	Luteolin -4'-*O*- hexoside
24 [b]	19.2	597.18097	597.18249	0.7	$C_{27}H_{33}O_{15}$	MS^2[597] 449.12878(3), 297.07602(1), 273.07608(100) ; MS^3[597→273] 167.1	Phloretin-4-*O*-glucosyl(1→6)glucoside
25[a b]	20.7	433.11337	433.11347	-1.5	$C_{21}H_{21}O_{10}$	MS^2[433]271.06046(100)	Naringin
26 [b]	21.5	463.08859	463.08820	0.8	$C_{21}H_{19}O_{12}$	MS^2[463]301.03488(100), 300.02670 (34); MS^3[463→301] 179.0 (100), 151.0 (69)	Quercetin 7-*O*- hexoside
27[ac]	21.6	567.17163	567.17193	-0.5	$C_{26}H_{31}O_{14}$	MS^2[567]419.11844 (14), 297.07605 (5), 273.07654(100), 167.03487(7); MS^3[567→273] 167.1(100)	Phloretin2-O-[β-D-apiofuranosyl(1→6)-β -D-glucopyranoside
28 [b]	21.7	581.18591	581.18758	-2.9	$C_{27}H_{33}O_{14}$	MS^2[581] 433.13397 (3), 297.07596 (1), 273.07593 (100), 167.03481(4)	Phloretin rhamnosyl(1→6) glucoside
29 [a]	22.2	463.08817	463.08820	-0.1	$C_{21}H_{19}O_{12}$	MS^2[463]301.03488 (100), 300.02692 (25); MS^3[463→301] 179.0 (100) ,151.1(73)	Quercetin 7-*O*-*β*-glucoside
30	23.2	433.07672	433.07709	-2.1	$C_{20}H_{17}O_{11}$	MS^2[433]301.03439(100), 300.02658(19); MS^3[433→301]283(19), 273(19), 257(14), 255(7), 193(7), 179(100), 151(71)	Quercetin-3-*O*-arabinfuranoside
31	23.8	433.07697	433.07709	-1.5	$C_{20}H_{17}O_{11}$	MS^2[433] 301.03452(92), 300.02670(100)	Quercetin-3-*O*- arabinpyranoside
32 [a]	24.2	435.12952	435.12967	-0.3	$C_{21}H_{23}O_{10}$	MS^2[435]273.07642 (100); MS^3[435→273] 167.0(100)	Phloridzin/ Phlorhizin
33 [b]	25.6	447.09344	447.09329	0.3	$C_{21}H_{19}O_{11}$	MS^2[447]327.05014(18), 285.04010(60), 284.03226(100), 255.02939 (2); MS^3[437→284] 256.1(17), 255.1(100)	Kaempferol-3-*O*-hexoside
34 [c]	26.2	723.19324	723.19306	0.3	$C_{36}H_{35}O_{16}$	MS^2[723]597.16034(33), 543.12878(92), 435.11230 (36), 391.08203 (100),	Unknown Phloretin conjugate

						287.05569(30), 273.07663(45)	
35	26.3	285.03986	285.03991	-2.1	$C_{15}H_9O_6$	MS^2[285]267.02927(17), 257.04480(51), 243.02934(30), 241.04991(67), 217.05020(50), 213.05525(35) 199.03966(100), 175.03981(65), 151.00352(38), 135.04507(20) 133.02934(14)	Luteolin
36[a]	26.6	447.09329	447.09274	0	$C_{21}H_{19}O_{11}$	MS^2[447]301.03491(100), 300.02667(26); MS^3[447→301] 179.0(100), 151.0(67)	Quercitrin
37[a]	27.2	447.09235	447.09274	-2.5	$C_{21}H_{19}O_{11}$	MS^2[447]327.05008(21), 285.03967(78), 284.03195(100), 255.02931(15) MS^3[447→285] 267.1 (18), 257.2 (39), 256.1(22), 255.1(100), 241.1(17), 239.1(7), 229.2(15), 227.2(10), 213.0(9),	Kaempferol -3-*O*-glucoside
38[b]	27.3	287.05560	287.05556	-1.8	$C_{15}H_{11}O_6$	MS^2[287] 151.00354 (100)	Eriodictyol
39[b]	27.3	447.09341	447.09329	0.3	$C_{21}H_{19}O_{11}$	MS^2[447]301.03488(100), 300.02667 (21); MS^3[447→301]179.0(100),151.0 (51)	Quercetin-*O*-rhamnoside
40[b]	28.5	493.13547	493.13515	1.8	$C_{23}H_{25}O_{12}$	MS^2[493]433.11264(10), 289.07120 (100);MS^3[493→289]271.2(77), 245.2(19), 167.2 (100), 125.0 (32)	3-hydroxy phloretin-2-*O*-acetyl hexoside
41	28.8	435.12881	435.12967	0.7	$C_{21}H_{23}O_{10}$	MS^2[435]297.07599(17), 273.07605 (100);MS^3[435→273] 167.0(100)	Trilobatin
42[b]	28.9	417.08212	417.08272	-1.4	$C_{20}H_{17}O_{10}$	MS^2[417]327.04999(11), 285.03970 (52), 284.03186(100);MS^3[417→284]256.1(17), 255.1(100), 227.1(10)	Kaempferol pyranarabinoside
43	29.5	289.07123	289.07176	-1.8	$C_{15}H_{13}O_6$	MS^2[289]271.06049(70), 245.08138(13), 167.03481(100), 125.02447(45)	3-hydroxy phloretin
44	29.6	477.13925	477.14024	-2.1	$C_{23}H_{25}O_{11}$	MS^2[477] 417.11826(16), 273.07623(100), 167.03494(6)	phloretin-2-*O*-acetyl hexoside
45[b]	29.9	493.13535	493.13515	1.5	$C_{23}H_{25}O_{12}$	MS^2[493]289.07144(100) MS^3[493→289]271.1(74), 244.9(40), 167.2(100)	3-hydroxyphloretin-4-*O*-acetyl hexoside
46[c]	30.3	521.13043	521.13006	1.8	$C_{24}H_{25}O_{13}$	MS^2[521]477.13943(100), 273.07605 (12);MS^3[521→477]435 (15), 273 (100), 178(17), 167(31)	Phloretin-2-*O*-malonyl hexoside
47[c]	31.5	551.17584	551.17647	-2.1	$C_{26}H_{31}O_{13}$	MS^2[551]493.13358(100), 435.12823(82), 417.11792(24), 273.07602(94);MS^3[551→435] 273(100)	Unknown Phloretin conjugate
48[a]	32.2	431.09833	431.09837	1.2	$C_{21}H_{19}O_{10}$	MS^2[431]:285.03998(100), 284.03198(29), 255.02936(2);MS^3[431→285]267(47), 257(100), 255.0(56), 241.1(32), 239.1(20), 229.1(50), 213.2 (25), 199.1(16), 197.2 (19), 163.0(17)	Afzelin
49[c]	32.9	551.17596	551.17701	1.4	$C_{26}H_{31}O_{13}$	MS^2[551]507.14981(45), 435.12900(97), 273.07645(100);MS^3[551→273] 167.1(100)	Phloridzin monoacetin 1

50[a]	33.0	301.03476	301.03538	0.1	$C_{15}H_9O_7$	MS^2[301]178.99832(100), 151.00357(80)	Quercetin
51[c]	33.5	521.12885	521.12952	-2.1	$C_{24}H_{25}O_{13}$	MS^2[521]477.13867(100), 297.07596(3), 273.07599 (41)	Phloridzin-4-*O*-malonyl hexoside
52[a]	33.8	271.06073	271.06120	-1.7	$C_{15}H_{11}O_5$	MS^2[271]177.01903(24), 151.00354(100)	Naringenin
53	34.0	477.13916	477.14024	1.0	$C_{23}H_{25}O_{11}$	MS^2[477]417.11816(17), 273.07617(100), 167.03491(6)	phloretin-4-*O*-acetyl hexoside
54[c]	34.6	721.17517	721.17686	-2.8	$C_{36}H_{33}O_{16}$	MS^2[721]559.12250(100), 541.11218 (12), 285.03952(7)	Unknown Phloretin conjugate
55[c]	34.9	551.17719	551.17701	0.3	$C_{26}H_{31}O_{13}$	MS^2[551]507.14981(38), 435.12912(100), 273.07648(77); MS^3[551→273] 167.1(100)	Phloridzin monoacetin 2
56[b]	35.2	477.14047	477.14024	1.6	$C_{23}H_{25}O_{11}$	MS^2[477]273.07642(100), 167.03482(4)	6" -*O* -Acetyltrilobatin
57[c]	35.6	521.16522	521.16645	-2.2	$C_{25}H_{29}O_{12}$	MS^2[521]503.15421(35), 491.15442 (7), 273.07599(100)	Unknown phloretin conjugate
58[a]	36.2	273.07718	273.07685	3.2	$C_{15}H_{13}O_5$	MS^2[273]167.03497(100), 125.02449(4), 123.04525(4)	Phloretin
59[a]	39.8	285.03986	285.04046	-2.2	$C_{15}H_9O_6$	MS^2[285]267.02945 (33), 257.04486 (98),243.02942 (100), 241.05013(60), 229.05011(98) 213.05527 (86), 185. 06058(86) 169.06567(93), 151.00352(99)	Kaempferol
60[c]	41.1	555.14972	555.15025	-1.9	$C_{28}H_{27}O_{12}$	MS^2[555]407.09729(3), 273.07602(100), 167.03479 (6)	Unknown Phloretin conjugate
61[c]	43.6	581.16498	581.16645	-2.5	$C_{30}H_{29}O_{12}$	MS^2[581]433.11282(3) 307.08151(6), 273.07602 (100); MS^3[581→273] 167.1	Phloretin-2-*O*-coumaroylhexoside
62[c]	44.2	611.17560	611.17701	-2.3	$C_{31}H_{31}O_{13}$	MS^2[611]463.12311(2), 337.09161(4), 273.07599(100); MS^3[611→273] 167.1	Phloretin-2-*O*- feruloylhexoside
63[c]	44.6	641.18591	641.18758	-2.6	$C_{32}H_{33}O_{14}$	MS^2[641]297.07602(20), 273.07602(100)	Phloretin-2-*O*-sinapoylhexoside
64[c]	44.9	581.16498	581.16645	-2.5	$C_{30}H_{29}O_{12}$	MS^2[581]433.11273(3), 307.08148(6), 273.07611(100); MS^3[581→273] 167.1	Phloretin-4-*O*-coumaroylhexoside
65[c]	45.2	641.18610	641.18758	-2.3	$C_{32}H_{33}O_{14}$	MS^2[641]273.07596(100), 493.13351(2), 367.10254 (6); MS^3[641→273] 167.1	Phloretin-4-*O*-sinapoylhexoside
66[c]	45.5	611.17578	611.17701	-2.0	$C_{31}H_{31}O_{13}$	MS^2[611]463.12292(2), 337.09174(3), 273.07599(100); MS^3[611→273] 167.1	Phloretin-4-*O*-feruloylhexoside
67[c]	49.1	601.22754	601.22905	-2.3	$C_{31}H_{37}O_{12}$	MS^2[601]273.07599 (100); MS^3[601→273] 167.0	Unknown Phloretin conjugate
68[c]	49.2	601.22760	601.22905	-2.4	$C_{31}H_{37}O_{12}$	MS^2[601]273.07599(100); MS^3[601→273] 167.0	Unknown Phloretin conjugate

[a]Compared with reference standards
[b]Firstly detected in this genus
[c]Identified as new compounds