Article

Identification of chemical profiles and biological properties of *Rhizophora racemosa* G. Mey. extracts obtained by different methods and solvents

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Chemical composition

Chemical compositions of the *R. racemosa* extracts were determined using a Dionex Ultimate 3000RS UHPLC instrument. The extracts were filtered through 0.22 μm PTFE syringe filter (Labex Ltd, Hungary) before HPLC analysis. The compounds were separated on a Thermo Accucore C18 (100 mm x 2.1, mm i. d., 2.6 μm) column thermostated at 25 °C (± 1 °C). The solvents used were water (A) and methanol (B), both were acidified with 0.1 % formic acid. The flow rate was maintained at 0.2 mL min^{-1}. The elution gradient was isocratic 5 % B (0-3 min), a linear gradient increasing from 5% B to 100% (3-43 min), 100% B (43-61 min), a linear gradient decreasing from 100% B to 5% (61-62 min) and 5% B (62-70 min). The column was coupled to a Thermo Q Exactive Orbitrap mass spectrometer (Thermo Scientific, USA) equipped with electrospray ionization source. MS spectra were recorded in positive and negative-ion mode, respectively.

Trace Finder 3.1 (Thermo Scientific, USA) software was applied for target screening. The compounds listed in the tables were identified on the basis our previous published works or data found in literature using exact molecular mass, isotopic pattern and characteristic fragment ions. In every case, the exact molecular mass, isotopic pattern, characteristic fragment ions and retention time were used for the identification of the compounds which are marked that were confirmed by standards.

Assays for Total Phenolic and Flavonoid Contents

The total phenolic content was determined by employing the methods given in the literature with some modification. Sample solution (0.25 mL) was mixed with diluted Folin–Ciocalteu reagent (1 mL, 1:9, v/v) and shaken vigorously. After 3 min, Na_2CO_3 solution (0.75 mL, 1%) was added and the sample absorbance was read at 760 nm after a 2 h incubation at room temperature. The total phenolic content was expressed as milligrams of gallic acid equivalents (mg GAE/g extract)[1].

The total flavonoid content was determined using the $AlCl_3$ method. Briefly, sample solution (1 mL) was mixed with the same volume of aluminum trichloride (2%) in methanol. Similarly, a blank was prepared by adding sample solution (1 mL) to methanol (1 mL) without $AlCl_3$. The sample and blank absorbances were read at 415 nm after a 10 min incubation at room temperature. The absorbance of the blank was subtracted from that of the sample. Rutin was used as a reference standard and the total flavonoid content was expressed as milligrams of rutin equivalents (mg RE/g extract) [1].

Determination of Antioxidant and Enzyme Inhibitory Effects

Antioxidant (DPPH and ABTS radical scavenging, reducing power (CUPRAC and FRAP), phosphomolybdenum and metal chelating (ferrozine method)) and enzyme inhibitory activities (cholinesterase (Elmann's method), tyrosinase (dopachrome method), α-amylase (iodine/potassium iodide method), α -glucosidase (chromogenic PNPG method) and pancreatic lipase (*p*-nitrophenyl butyrate (p-NPB) method) were determined using the methods previously described by Uysal et al. [1] and Grochowski et al. [2]

For the DPPH (1,1-diphenyl-2-picrylhydrazyl) radical scavenging assay: Sample solution was added to 4 mL of a 0.004% methanol solution of DPPH. The sample absorbance was read at 517 nm after a 30 min incubation at room temperature in the dark. DPPH radical scavenging activity was expressed as milligrams of trolox equivalents (mg TE/g extract).

For ABTS (2,2′-azino-bis(3-ethylbenzothiazoline) 6-sulfonic acid) radical scavenging assay: Briefly, ABTS+ was produced directly by reacting 7 mM ABTS solution with 2.45 mM potassium persulfate and allowing the mixture to stand for 12–16 in the dark at room temperature. Prior to beginning the assay, ABTS solution was diluted with methanol to an absorbance of 0.700 ± 0.02 at 734 nm. Sample solution was added to ABTS solution (2 mL) and mixed. The sample absorbance was read at 734 nm after a 30 min incubation at room temperature. The ABTS radical scavenging activity was expressed as milligrams of trolox equivalents (mg TE/g extract).

For CUPRAC (cupric ion reducing activity) activity assay: Sample solution was added to premixed reaction mixture containing $CuCl_2$ (1 mL, 10 mM), neocuproine (1

mL, 7.5 mM) and NH_4Ac buffer (1 mL, 1 M, pH 7.0). Similarly, a blank was prepared by adding sample solution (0.5 mL) to premixed reaction mixture (3 mL) without $CuCl_2$. Then, the sample and blank absorbances were read at 450 nm after a 30 min incubation at room temperature. The absorbance of the blank was subtracted from that of the sample. CUPRAC activity was expressed as milligrams of trolox equivalents (mg TE/g extract).

For FRAP (ferric reducing antioxidant power) activity assay: Sample solution was added to premixed FRAP reagent (2 mL) containing acetate buffer (0.3 M, pH 3.6), 2,4,6-tris(2-pyridyl)-S-triazine (TPTZ) (10 mM) in 40 mM HCl and ferric chloride (20 mM) in a ratio of 10:1:1 (v/v/v). Then, the sample absorbance was read at 593 nm after a 30 min incubation at room temperature. FRAP activity was expressed as milligrams of trolox equivalents (mg TE/g extract).

For phosphomolybdenum method: Sample solution was combined with 3 mL of reagent solution (0.6 M sulfuric acid, 28 mM sodium phosphate and 4 mM ammonium molybdate). The sample absorbance was read at 695 nm after a 90 min incubation at 95 °C. The total antioxidant capacity was expressed as millimoles of trolox equivalents (mmol TE/g extract).

For metal chelating activity assay: Briefly, sample solution was added to $FeCl_2$ solution (0.05 mL, 2 mM). The reaction was initiated by the addition of 5 mM ferrozine (0.2 mL). Similarly, a blank was prepared by adding sample solution (2 mL) to $FeCl_2$ solution (0.05 mL, 2 mM) and water (0.2 mL) without ferrozine. Then, the sample and blank absorbances were read at 562 nm after 10 min incubation at room temperature. The absorbance of the blank was sub-tracted from that of the sample. The metal

chelating activity was expressed as milligrams of EDTA (disodium edetate) equivalents (mg EDTAE/g extract).

For Cholinesterase (ChE) inhibitory activity assay: Sample solution (was mixed with DTNB (5,5-dithio-bis(2-nitrobenzoic) acid, Sigma, St. Louis, MO, USA) (125 µL) and AChE (acetylcholines-terase (Electric ell acetylcholinesterase, Type-VI-S, EC 3.1.1.7,Sigma)), or BChE (butyrylcholinesterase (horse serum butyrylcholinesterase, EC 3.1.1.8, Sigma)) solution (25 µL) in Tris–HCl buffer (pH 8.0) in a 96-well microplate and incubated for 15 min at 25 °C. The reaction was then initiated with the addition of acetylthiocholine iodide (ATCI, Sigma) or butyrylthiocholine chloride (BTCl, Sigma) (25 µL). Similarly, a blank was prepared by adding sample solution to all reaction reagents without enzyme (AChE or BChE) solution. The sample and blank absorbances were read at 405 nm after 10 min incubation at 25 °C. The absorbance of the blank was subtracted from that of the sample and the cholinesterase inhibitory activity was expressed as galanthamine equivalents (mgGALAE/g extract).

For Tyrosinase inhibitory activity assay: Sample solution was mixed with tyrosinase solution (40 µL, Sigma) and phosphate buffer (100 µL, pH 6.8) in a 96-well microplate and incubated for 15 min at 25 °C. The reaction was then initiated with the addition of L-DOPA (40 µL, Sigma). Similarly, a blank was prepared by adding sample solution to all reaction reagents without enzyme (tyrosinase) solution. The sample and blank absorbances were read at 492 nm after a 10 min incubation at 25 °C. The absorbance of the blank was subtracted from that of the sample and the tyrosinase inhibitory activity was expressed as kojic acid equivalents (mgKAE/g extract).

For α-amylase inhibitory activity assay: Sample solution was mixed with α-amylase solution (ex-porcine pancreas, EC 3.2.1.1, Sigma) (50 µL) in phosphate buffer

(pH 6.9 with 6 mM sodium chloride) in a 96-well microplate and incubated for 10 min at 37 °C. After pre-incubation, the reaction was initiated with the addition of starch solution (50 µL, 0.05%). Similarly, a blank was prepared by adding sample solution to all reaction reagents without enzyme (α-amylase) solution. The reaction mixture was incubated 10 min at 37 °C. The reaction was then stopped with the addition of HCl (25 µL, 1 M). This was followed by addition of the iodine-potassium iodide solution (100 µL). The sample and blank absorbances were read at 630 nm. The absorbance of the blank was subtracted from that of the sample and the α-amylase inhibitory activity was expressed as acarbose equivalents (mmol ACE/g extract).

For α-glucosidase inhibitory activity assay: Sample solution was mixed with glutathione (50 µL), α-glucosidase solution (from Saccharomyces cerevisiae, EC 3.2.1.20, Sigma) (50 µL) in phosphate buffer (pH 6.8) and PNPG (4-N-trophenyl-α-D-glucopyranoside, Sigma) (50 µL) in a 96-well microplate and incubated for 15 min at 37 °C. Similarly, a blank was prepared by adding sample solution to all reaction reagents without enzyme (α-glucosidase) solution. The reaction was then stopped with the addition of sodium carbonate (50 µL, 0.2 M). The sample and blank absorbances were read at 400 nm. The absorbance of the blank was subtracted from that of the sample and the α-glucosidase inhibitory activity was expressed as acarbose equivalents (mmol ACE/g extract).

Table S1. Chemical composition in the infusion of leaves

No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1[1]	Gallic acid (3,4,5-Trihydroxybenzoic acid)	C7H6O5	2,49		169,01370	125,0230	97,0281	81,0331	69,0330	
2	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,50		153,01879	109,0280	108,0203	91,0176	81,0330	
3	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,24	355,10291		163,0389	145,0284	135,0442	117,0337	89,0389
4	Hydroxybenzaldehyde	C7H6O2	13,08	123,04461		105,0451	95,0496	81,0704	67,0549	53,0394
5	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,30		337,09235	191,0553	173,0447	163,0389	119,0488	93,0330
6[1]	Catechin	C15H14O6	14,00		289,07121	245,0816	205,0499	203,0706	125,0230	109,0280
7	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,73	179,03444		151,0385	133,0285	123,0442	105,0337	89,0390
8[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,88	355,10291		163,0389	145,0284	135,0441	117,0337	89,0389
9	3-O-Feruloylquinic acid	C17H20O9	15,13		367,10291	193,0499	191,0539	173,0439	134,0361	
10	Caffeic acid	C9H8O4	15,19		179,03444	135,0438	107,0487			
11	Procyanidin B	C30H26O12	15,69		577,13460	451,1032	425,0884	407,0771	289,0720	125,0230
12	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,15	355,10291		163,0389	145,0284	135,0442	117,0337	89,0389
13	Cinchonain II isomer 1	C39H32O15	17,04		739,16630	339,0515	289,0707	177,0187		
14	2-Oxindole	C8H7NO	17,23	134,06059		106,0655	105,0338	79,0548		
15	Procyanidin C	C45H38O18	17,33		865,19799	695,1398	577,1348	407,0768	289,0720	125,0230
16	5-O-(4-Coumaroyl)quinic acid	C16H18O8	17,45		337,09235	191,0553	173,0444	163,0389	119,0488	93,0330
17[1]	Epicatechin	C15H14O6	17,61		289,07121	245,0817	205,0498	203,0708	125,0230	109,0281
18	Cinchonain II isomer 2	C39H32O15	17,91		739,16630	587,1152	339,0512	289,0725	177,0182	
19	Cinchonain II isomer 3	C39H32O15	18,09		739,16630	587,1201	339,0500	289,0728	177,0182	
20	4-O-(4-Coumaroyl)quinic acid	C16H18O8	18,10		337,09235	191,0554	173,0444	163,0389	119,0488	93,0330
21	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,50	185,08139		170,0577	154,0623	153,0546	139,0389	125,0598
22	5-O-Feruloylquinic acid	C17H20O9	18,51		367,10291	193,0495	191,0553	173,0443	134,0362	93,0329
23[1]	4-Coumaric acid	C9H8O3	18,54		163,03952	119,0488	93,0329			
24	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,77		225,11269	181,1227	165,0903	147,0801	135,0804	59,0123
25	4-O-Feruloylquinic acid	C17H20O9	19,02		367,10291	193,0499	191,0553	173,0445	134,0365	93,0329
26	Riboflavin	C17H20N4O6	19,09	377,14611		359,1353	243,0877	172,0867	99,0445	69,0341
27	Naringenin-C-hexoside isomer 1	C21H22O10	19,84	435,12913		399,1093	339,0859	315,0850	285,0756	195,0291
28[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,91		303,05048	285,0402	175,0386	153,0181	125,0229	57,0331
29	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,29		771,19839	301,0356	300,0277	299,0198	271,0249	255,0297
30	Naringenin-C-hexoside isomer 2	C21H22O10	20,39	435,12913		399,1060	339,0866	315,0868	285,0761	195,0290

31	Quercetin-O-hexosylhexoside	C27H30O17	20,70		625,14048	301,0356	300,0276	299,0198	271,0249	255,0296
32	Naringenin-C-hexoside isomer 3	C21H22O10	20,74	435,12913		417,1191	369,0981	339,0870	219,0285	195,0289
33	Quercetin-O-dirhamnosylhexoside	C33H40O20	21,28		755,20347	301,0355	300,0276	299,0190	271,0248	255,0296
34	Hexahydroxy(iso)flavone-O-hexoside	C21H20O13	21,47		479,08257	316,0228	287,0187	271,0247		
35	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,56		625,14048	317,0299	316,0225	315,0175	287,0201	271,0250
36[1]	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,89	433,11348		415,1024	397,0918	367,0809	313,0705	283,0600
37	Kaempferol-O-dirhamnosylhexoside	C33H40O19	22,59		739,20856	285,0406	284,0328	283,0243	255,0297	227,0343
38	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,78	433,11348		415,1016	397,0918	337,0706	313,0705	283,0601
39[1]	Naringin (Naringenin-7-O-neohesperidoside)	C27H32O14	23,45		579,17139	459,1155	271,0613	151,0022	119,0487	
40[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,53	611,16122		465,1033	303,0495	129,0546	85,0288	71,0497
41	Quercetin-O-pentoside	C20H18O11	23,79		433,07709	301,0346	300,0279	271,0242	255,0299	151,0026
42	Astragalin (Kaempferol-3-O-glucoside)	C21H20O11	25,29		447,09274	300,0275	285,0405	284,0328	271,0250	255,0297
43	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,41		593,15065	327,0512	285,0406	284,0328	255,0296	227,0343
44[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,50		287,05556	151,0023	135,0440	125,0227	107,0123	
45	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,76		623,16122	315,0514	314,0432	300,0277	299,0198	271,0248
46	Abscisic acid	C15H20O4	25,88		263,12834	219,1385	204,1149	201,1276	152,0830	151,0753
47[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,57		301,03483	273,0411	178,9976	151,0024	121,0281	107,0124
48[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,80		271,06069	177,0179	165,0188	151,0025	119,0487	107,0123
49[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,44		285,03991	175,0391	151,0025	149,0237	133,0283	
50[1]	Kaempferol (3,4',5,7-Tetrahydroxyflavone)	C15H10O6	29,93		285,03991	257,0468	229,0502	213,0555	151,0021	

Table S2. Chemical composition in the ethyl acetate (HAE) of leaves

No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,56		153,01879	109,0280	108,0203	91,0176	81,0330	
2	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,29	355,10291		163,0389	145,0285	135,0442	117,0337	89,0390
3	Hydroxybenzaldehyde	C7H6O2	13,07	123,04461		105,0451	95,0496	81,0702	67,0548	53,0394
4	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,31		337,09235	191,0553	173,0447	163,0388	119,0487	
5	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,75	179,03444		151,0390	133,0284	123,0442	105,0341	
6[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,90	355,10291		163,0389	145,0285	135,0442	117,0336	89,0389
7	Caffeic acid	C9H8O4	15,17		179,03444	135,0439	107,0489			
8	Procyanidin B	C30H26O12	15,69		577,13460	451,1028	425,0863	407,0771	289,0720	125,0228
9	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,17	355,10291		163,0390	145,0285	135,0443	117,0338	89,0389
10	2-Oxindole	C8H7NO	17,22	134,06059		106,0655	105,0338	79,0548		
11	Procyanidin C	C45H38O18	17,31		865,19790	695,1354	577,1348	407,0773	289,0711	125,0229
12	5-O-(4-Coumaroyl)quinic acid	C16H18O8	17,43		337,09235	191,0552	173,0436	163,0387	119,0488	93,0330
13[1]	Epicatechin	C15H14O6	17,59		289,07121	245,0818	205,0502	203,0707	125,0229	109,0280
14	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,46	185,08139		170,0575	154,0624	153,0546	139,0391	125,0598
15[1]	4-Coumaric acid	C9H8O3	18,49		163,03952	119,0487	93,0331			
16	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,72		225,11269	181,1227	165,0910	147,0802	135,0802	59,0122
17[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,88		303,05048	285,0406	175,0390	153,0179	125,0229	57,0329
18	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,23		771,19839	301,0357	300,0277	299,0197	271,0249	255,0296
19	Quercetin-O-hexosylhexoside	C27H30O17	20,65		625,14048	301,0353	300,0277	299,0213	271,0247	255,0295
20	Quercetin-O-dirhamnosylhexoside	C33H40O20	21,24		755,20347	301,0356	300,0276	299,0195	271,0248	255,0296
21	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,51		625,14048	317,0310	316,0225	287,0191	271,0252	
22[1]	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,86	433,11348		415,1015	397,0919	367,0808	313,0705	283,0598
23	Kaempferol-O-dirhamnosylhexoside	C33H40O19	22,56		739,20856	285,0406	284,0328	283,0255	255,0297	227,0344
24	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,77	433,11348		415,1008	397,0918	337,0706	313,0706	283,0599
25[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,55	611,16122		465,1025	303,0498	129,0549	85,0289	71,0497
26	Quercetin-O-pentoside	C20H18O11	23,77		433,07709	301,0349	300,0277	271,0246	255,0304	151,0029
27	Astragalin (Kaempferol-3-O-glucoside)	C21H20O11	25,26		447,09274	300,0278	285,0407	284,0329	271,0249	255,0297
28	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,38		593,15065	327,0512	285,0405	284,0327	255,0296	227,0343
29[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,46		287,05556	269,0462	151,0024	135,0439	125,0230	107,0123
30	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,74		623,16122	315,0515	314,0430	300,0270	299,0212	271,0238

31	Abscisic acid	C15H20O4	25,86		263,12834	219,1383	204,1150	201,1270	152,0827	151,0748
32[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,56		301,03483	273,0409	178,9976	151,0024	121,0280	107,0124
33[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,78		271,06069	177,0179	165,0188	151,0024	119,0487	107,0124
34[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,43		285,03991	175,0391	151,0025	149,0235	133,0281	
35[1]	Kaempferol (3,4',5,7-Tetrahydroxyflavone)	C15H10O6	29,92		285,03991	257,0449	229,0501	213,0552	151,0026	
36[1]	Apigenin (4',5,7-Trihydroxyflavone)	C15H10O5	30,27		269,04500	225,0553	201,0551	151,0022	149,0231	117,0330
37[1]	Isorhamnetin (3'-Methoxy-3,4',5,7-tetrahydroxyflavone)	C16H12O7	30,40		315,05048	300,0275	283,0273	164,0104	151,0025	107,0124
38	Methoxy-trihydroxy(iso)flavone	C16H12O6	30,48		299,05556	284,0329	256,0375			
39	Pinocembrin (5,7-Dihydroxyflavanone)	C15H12O4	32,77		255,06573	213,0553	151,0024	145,0646	107,0126	65,0019

Table S3. Chemical composition in the methanol (HAE) of leaves

No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,53		153,01879	109,0280	108,0202	91,0175	81,0330	
2	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,28	355,10291		163,0390	145,0286	135,0443	117,0338	89,0390
3	Hydroxybenzaldehyde	C7H6O2	13,08	123,04461		105,0453	95,0497	81,0704	67,0549	53,0394
4	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,33		337,09235	191,0555	173,0440	163,0389	119,0488	93,0330
5[1]	Catechin	C15H14O6	14,02		289,07121	245,0817	205,0501	203,0708	125,0230	109,0281
6	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,74	179,03444		151,0392	133,0286	123,0443	105,0339	89,0392
7[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,88	355,10291		163,0390	145,0286	135,0443	117,0338	89,0390
8	3-O-Feruloylquinic acid	C17H20O9	15,13		367,10291	193,0499	191,0539	173,0445	134,0362	
9	Caffeic acid	C9H8O4	15,17		179,03444	135,0439	107,0488			
10	Procyanidin B	C30H26O12	15,69		577,13460	451,1036	425,0882	407,0772	289,0720	125,0230
11	Cinchonain II isomer 1	C39H32O15	16,08		739,16630	587,1197	339,0512	289,0723	177,0184	
12	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,15	355,10291		163,0390	145,0285	135,0442	117,0338	89,0390
13	Cinchonain II isomer 2	C39H32O15	17,04		739,16630	587,1196	339,0508	289,0721	177,0183	
14	2-Oxindole	C8H7NO	17,21	134,06059		106,0655	105,0339	79,0548		
15	Procyanidin C	C45H38O18	17,26		865,19799	695,1426	577,1357	407,0772	289,0721	125,0230
16	5-O-(4-Coumaroyl)quinic acid	C16H18O8	17,44		337,09235	191,0554	173,0439	163,0388	119,0486	93,0331
17[1]	Epicatechin	C15H14O6	17,58		289,07121	245,0817	205,0502	203,0708	125,0229	109,0280
18	Cinchonain II isomer 3	C39H32O15	17,87		739,16630	587,1212	339,0509	289,0723	177,0182	
19	4-O-(4-Coumaroyl)quinic acid	C16H18O8	18,07		337,09235	191,0561	173,0444	163,0389	119,0487	93,0330
20	Cinchonain II isomer 4	C39H32O15	18,07		739,16630	587,1216	339,0510	289,0718	177,0182	
21	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,46	185,08139		170,0576	154,0625	153,0547	139,0390	125,0599
22	5-O-Feruloylquinic acid	C17H20O9	18,48		367,10291	193,0506	191,0554	173,0443	134,0363	93,0332
23[1]	4-Coumaric acid	C9H8O3	18,49		163,03952	119,0488	93,0332			
24	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,73		225,11269	181,1221	165,0908	147,0804	135,0803	59,0123
25	4-O-Feruloylquinic acid	C17H20O9	18,97		367,10291	193,0499	191,0553	173,0444	134,0359	93,0330
26	Riboflavin	C17H20N4O6	19,06	377,14611		359,1353	243,0877	172,0868	99,0445	69,0342
27	Cinchonain I isomer 1	C24H20O9	19,30		451,10291	341,0666	289,0720	231,0294	217,0137	189,0185
28	Naringenin-C-hexoside isomer 1	C21H22O10	19,80	435,12913		399,1041	339,0867	315,0847	285,0764	195,0291

29[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,88		303,05048	285,0407	175,0388	153,0181	125,0229	57,0332
30	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,24		771,19839	301,0355	300,0277	299,0206	271,0248	255,0298
31	Naringenin-C-hexoside isomer 2	C21H22O10	20,36	435,12913		399,1061	339,0869	315,0855	285,0756	195,0290
32	Quercetin-O-hexosylhexoside	C27H30O17	20,66		625,14048	301,0356	300,0277	299,0209	271,0249	255,0297
33	Naringenin-C-hexoside isomer 3	C21H22O10	20,71	435,12913		417,1189	369,0970	339,0866	219,0292	195,0290
34	Quercetin-O-dirhamnosylhexoside	C33H40O20	21,26		755,20347	301,0353	300,0277	299,0201	271,0249	255,0298
35	Hexahydroxy(iso)flavone-O-hexoside	C21H20O13	21,44		479,08257	317,0302	316,0226	287,0197	271,0253	
36	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,53		625,14048	317,0304	316,0224	315,0159	287,0200	271,0249
37	Cinchonain I isomer 2	C24H20O9	21,70		451,10291	341,0666	289,0723	231,0295	217,0137	189,0186
38	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,85	433,11348		415,1024	397,0920	367,0816	313,0707	283,0601
39[1]	Kaempferol-O-dirhamnosylhexoside	C33H40O19	22,58		739,20856	285,0406	284,0328	283,0250	255,0297	227,0345
40	Cinchonain I isomer 3	C24H20O9	22,71		451,10291	341,0666	289,0705	231,0293	217,0137	189,0186
41	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,77	433,11348		415,1021	397,0919	337,0707	313,0706	283,0601
42[1]	Naringin (Naringenin-7-O-neohesperidoside)	C27H32O14	23,42		579,17139	459,1144	271,0610	151,0024	119,0492	
43[1]	Isoquercitrin (Quercetin-3-O-glucoside)	C21H20O12	23,43		463,08765	301,0357	300,0277	271,0249	255,0300	151,0024
44[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,52	611,16122		465,1016	303,0499	129,0549	85,0289	71,0497
45	Quercetin-O-pentoside	C20H18O11	23,79		433,07709	301,0356	300,0279	271,0246	255,0296	151,0032
46	Astragalin (Kaempferol-3-O-glucoside)	C21H20O11	25,28		447,09274	300,0276	285,0407	284,0329	271,0245	255,0298
47	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,39		593,15065	327,0519	285,0406	284,0328	255,0297	227,0344
48	Cinchonain I isomer 4	C24H20O9	25,44		451,10291	341,0667	289,0717	231,0294	217,0137	189,0185
49[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,47		287,05556	151,0024	135,0439	125,0230	107,0124	
50[1]	Isorhamnetin-3-O-glucoside	C22H22O12	25,50		477,10330	314,0434	299,0187	285,0404	271,0244	243,0301
51	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,75		623,16122	315,0514	314,0437	300,0280	299,0199	271,0251
52	Abscisic acid	C15H20O4	25,87		263,12834	219,1385	204,1151	201,1278	152,0831	151,0752
53[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,56		301,03483	273,0402	178,9976	151,0024	121,0281	107,0125
54[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,79		271,06069	177,0182	165,0182	151,0025	119,0488	107,0125
55[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,43		285,03991	217,0493	175,0389	151,0025	149,0232	133,0282
56[1]	Kaempferol (3,4',5,7-Tetrahydroxyflavone)	C15H10O6	29,92		285,03991	257,0445	229,0502	213,0549	169,0647	151,0021
57[1]	Apigenin (4',5,7-Trihydroxyflavone)	C15H10O5	30,29		269,04500	225,0546	201,0551	151,0025	149,0232	117,0331
58[1]	Isorhamnetin (3'-Methoxy-3,4',5,7-tetrahydroxyflavone)	C16H12O7	30,42		315,05048	300,0279	283,0273	164,0104	151,0026	107,0124
59	Methoxy-trihydroxy(iso)flavone	C16H12O6	30,49		299,05556	284,0321	256,0366			
60	Pinocembrin (5,7-Dihydroxyflavanone)	C15H12O4	32,77		255,06573	213,0548	151,0032	145,0646	107,0126	

Table S4. Chemical composition in the infusion of bark

No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1[1]	Gallic acid (3,4,5-Trihydroxybenzoic acid)	C7H6O5	2,58		169,01370	125,0230	97,0280	81,0331	69,0330	
2	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,48		153,01879	109,0280	108,0203	91,0174	81,0331	
3	Pantothenic acid	C9H17NO5	6,10	220,11850		202,1077	184,0972	174,1131	116,0347	90,0555
4	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,12	355,10291		163,0391	145,0286	135,0443	117,0339	89,0391
5	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,29		337,09235	191,0554	173,0446	163,0389	119,0488	93,0329
6[1]	Catechin	C15H14O6	14,01		289,07121	245,0819	205,0503	203,0709	125,0231	109,0281
7	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,72	179,03444		151,0390	133,0286	123,0444	105,0341	
8[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,86	355,10291		163,0391	145,0286	135,0443	117,0339	89,0390
9	3-O-Feruloylquinic acid	C17H20O9	15,10		367,10291	193,0500	191,0558	173,0424	134,0361	
10	Caffeic acid	C9H8O4	15,18		179,03444	135,0439	107,0488			
11	Procyanidin B	C30H26O12	15,67		577,13460	451,1034	425,0881	407,0774	289,0722	125,0230
12	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,12	355,10291		163,0391	145,0286	135,0443	117,0339	89,0391
13	Cinchonain II isomer 1	C39H32O15	17,03		739,16630	587,1199	339,0523	289,0711	177,0183	
14	2-Oxindole	C8H7NO	17,22	134,06059		106,0656	105,0341	79,0549		
15	Procyanidin C	C45H38O18	17,31		865,19799	695,1422	577,1364	407,0772	289,0721	125,0230
16	5-O-(4-Coumaroyl)quinic acid	C16H18O8	17,43		337,09235	191,0555	173,0444	163,0388	119,0487	93,0331
17[1]	Epicatechin	C15H14O6	17,58		289,07121	245,0818	205,0503	203,0708	125,0230	109,0281
18	Cinchonain II isomer 2	C39H32O15	17,89		739,16630	587,1217	339,0515	289,0719	177,0181	
19	4-O-(4-Coumaroyl)quinic acid	C16H18O8	18,07		337,09235	191,0556	173,0445	163,0389	119,0488	93,0330
20	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,47	185,08139		170,0574	154,0625	153,0547	139,0390	125,0599
21	5-O-Feruloylquinic acid	C17H20O9	18,48		367,10291	193,0502	191,0554	173,0441	134,0357	93,0331
22[1]	4-Coumaric acid	C9H8O3	18,51		163,03952	119,0488	93,0331			
23	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,75		225,11269	181,1221	165,0906	147,0803	135,0800	59,0123
24	4-O-Feruloylquinic acid	C17H20O9	18,98		367,10291	193,0501	191,0553	173,0446	134,0360	93,0333
25	Riboflavin	C17H20N4O6	19,07	377,14611		359,1358	243,0879	172,0870	99,0449	69,0343
26	Naringenin-C-hexoside isomer 1	C21H22O10	19,81	435,12913		399,1052	339,0870	315,0877	285,0760	195,0293
27[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,89		303,05048	285,0409	175,0387	153,0180	125,0230	57,0332

28	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,25		771,19839	301,0356	300,0279	299,0204	271,0251	255,0299
29	Naringenin-C-hexoside isomer 2	C21H22O10	20,35	435,12913		399,1085	339,0870	315,0857	285,0757	195,0291
30	Quercetin-O-hexosylhexoside	C27H30O17	20,67		625,14048	301,0353	300,0279	299,0204	271,0250	255,0299
31	Naringenin-C-hexoside isomer 3	C21H22O10	20,71	435,12913		417,1179	369,0976	339,0849	219,0288	195,0292
32	Quercetin-O-dirhamnosylhexoside	C33H40O20	21,26		755,20347	301,0352	300,0280	299,0201	271,0244	255,0298
33	Hexahydroxy(iso)flavone-O-hexoside	C21H20O13	21,44		479,08257	317,0327	316,0235	287,0195	271,0248	
34	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,52		625,14048	317,0305	316,0227	315,0151	287,0201	271,0250
35[1]	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,85	433,11348		415,1028	397,0921	367,0815	313,0708	283,0603
36	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,75	433,11348		415,1027	397,0920	337,0709	313,0707	283,0603
37	Luteolin-7-O-glucoside (Cynaroside)	C21H20O11	22,86		447,09274	327,0506	285,0409	284,0330	151,0026	133,0278
39[1]	Isoquercitrin (Quercetin-3-O-glucoside)	C21H20O12	23,44		463,08765	301,0358	300,0278	271,0251	255,0300	151,0024
38[1]	Naringin (Naringenin-7-O-neohesperidoside)	C27H32O14	23,45		579,17139	459,1178	271,0617	151,0024	119,0489	
40	Luteolin-7-O-rutinoside (Scolymoside)	C27H30O15	23,50		593,15065	447,0928	285,0408	284,0331	151,0024	133,0283
41[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,52	611,16122		465,1032	303,0501	129,0550	85,0290	71,0498
42	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,38		593,15065	327,0506	285,0407	284,0329	255,0298	227,0342
43[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,45		287,05556	151,0024	135,0439	125,0234	107,0123	
44[1]	Isorhamnetin-3-O-glucoside	C22H22O12	25,45		477,10330	314,0443	299,0193	285,0399	271,0252	243,0293
45	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,72		623,16122	315,0515	314,0435	300,0281	299,0206	271,0252
46	Abscisic acid	C15H20O4	25,84		263,12834	219,1386	204,1150	201,1279	152,0830	151,0753
47	Tetrahydroxyxanthone	C13H8O6	26,77		259,02427	231,0301	215,0346	203,0347	187,0389	
48[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,54		301,03483	273,0400	178,9976	151,0026	121,0281	107,0126
49[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,77		271,06069	177,0190	165,0183	151,0025	119,0488	107,0124
50[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,42		285,03991	217,0504	175,0391	151,0025	149,0235	133,0282
51	Methoxy-tetrahydroxy(iso)flavone	C16H12O7	28,50		315,05048	300,0278	299,0212			
52[1]	Apigenin (4',5,7-Trihydroxyflavone)	C15H10O5	30,26		269,04500	225,0553	201,0551	151,0025	149,0232	117,0331
53	Methoxy-trihydroxy(iso)flavone isomer 1	C16H12O6	30,48		299,05556	284,0329	256,0373			
54	Methoxy-trihydroxy(iso)flavone isomer 2	C16H12O6	30,93		299,05556	284,0331	256,0376	255,0306	227,0343	

Table S5. Chemical composition in the ethyl acetate (HAE) of bark

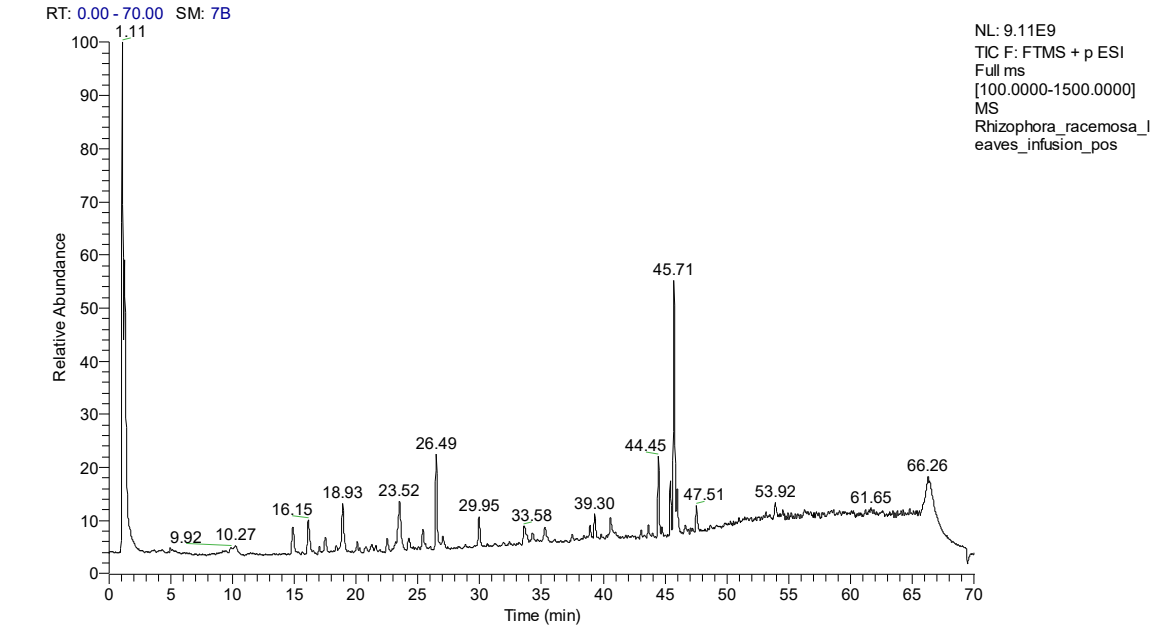
No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,53		153,01879	109,0281	108,0203	91,0174	81,0333	
2	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,25	355,10291		163,0391	145,0283	135,0443	117,0341	
3	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,30		337,09235	191,0534	173,0446	163,0391	119,0489	
4[1]	Catechin	C15H14O6	14,02		289,07121	245,0812	205,0506	203,0715	125,0229	109,0283
5	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,70	179,03444		151,0393	133,0285	123,0444	105,0342	
6[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,88	355,10291		163,0391	145,0286	135,0443	117,0340	89,0390
7	Caffeic acid	C9H8O4	15,17		179,03444	135,0440	107,0490			
8	Procyanidin B	C30H26O12	15,68		577,13460	451,1003	425,0888	407,0774	289,0720	125,0231
9	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,12	355,10291		163,0392	145,0286	135,0444	117,0342	89,0391
10	2-Oxindole	C8H7NO	17,19	134,06059		106,0656	105,0341	79,0550		
11	Procyanidin C	C45H38O18	17,29		865,19799	695,1467	577,1313	407,0764	289,0728	125,0231
12[1]	Epicatechin	C15H14O6	17,56		289,07121	245,0813	205,0497	203,0716	125,0232	109,0281
13	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,44	185,08139		170,0574	154,0626	153,0548	139,0392	125,0600
14[1]	4-Coumaric acid	C9H8O3	18,50		163,03952	119,0489	93,0330			
15	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,74		225,11269	181,1221	165,0909	147,0806	135,0800	59,0123
16	Cinchonain I isomer 1	C24H20O9	19,29		451,10291	341,0671	289,0720	231,0292	217,0143	189,0185
17[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,88		303,05048	285,0411	175,0389	153,0179	125,0230	57,0331
18	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,25		771,19839	301,0367	300,0282	299,0204	271,0245	255,0300
19	Quercetin-O-hexosylhexoside	C27H30O17	20,66		625,14048	301,0353	300,0283	299,0204	271,0231	255,0292
20	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,53		625,14048	317,0305	316,0225	315,0151	287,0201	271,0244
21	Cinchonain I isomer 2	C24H20O9	21,67		451,10291	341,0678	289,0720	231,0292	217,0137	189,0181
22[1]	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,86	433,11348		415,1026	397,0923	367,0817	313,0710	283,0600
23	Cinchonain I isomer 3	C24H20O9	22,71		451,10291	341,0667	289,0720	231,0283	217,0132	189,0192
24	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,75	433,11348		415,1043	397,0917	337,0714	313,0710	283,0601
25[1]	Naringin (Naringenin-7-O-neohesperidoside)	C27H32O14	23,45		579,17139	459,1178	271,0610	151,0027	119,0486	
26[1]	Isoquercitrin (Quercetin-3-O-glucoside)	C21H20O12	23,46		463,08765	301,0357	300,0278	271,0250	255,0301	151,0024
27[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,52	611,16122		465,1047	303,0502	129,0550	85,0290	71,0498
28	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,38		593,15065	327,0506	285,0409	284,0330	255,0305	227,0346
29	Cinchonain I isomer 4	C24H20O9	25,40		451,10291	341,0664	289,0720	231,0287	217,0132	189,0188
30[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,45		287,05556	151,0025	135,0440	125,0234	107,0126	
31	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,71		623,16122	315,0513	314,0439	300,0279	299,0200	271,0267
32	Abscisic acid	C15H20O4	25,83		263,12834	219,1383	204,1149	201,1282	152,0832	151,0750
33[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,54		301,03483	273,0412	178,9977	151,0025	121,0281	107,0125
34[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,76		271,06069	177,0184	165,0183	151,0025	119,0489	107,0125
35[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,41		285,03991	217,0503	175,0388	151,0025	149,0233	133,0282
36[1]	Apigenin (4',5,7-Trihydroxyflavone)	C15H10O5	30,26		269,04500	225,0568	201,0551	151,0028	149,0230	117,0331

37[1]	Isorhamnetin (3'-Methoxy-3,4',5,7-tetrahydroxyflavone)	C16H12O7	30,39		315,05048	300,0283	283,0273	164,0108	151,0024	107,0125
38	Methoxy-trihydroxy(iso)flavone	C16H12O6	30,46		299,05556	284,0333	256,0377			

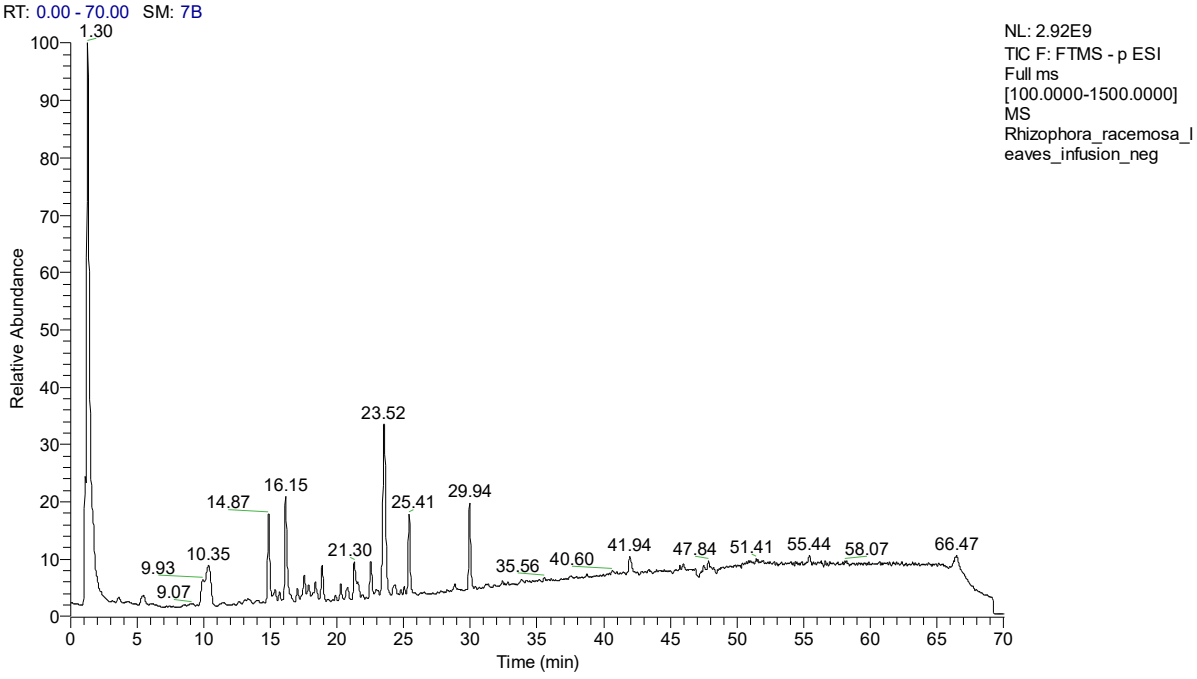
Table S6. Chemical composition in the methanol (HAE) of bark

No.	Name	Formula	Rt	$[M + H]^+$	$[M - H]^-$	Fragment 1	Fragment 2	Fragment 3	Fragment 4	Fragment 5
1[1]	Gallic acid (3,4,5-Trihydroxybenzoic acid)	C7H6O5	2,64		169,01370	125,0231	97,0281	81,0331	69,0332	
2	Protocatechuic acid (3,4-Dihydroxybenzoic acid)	C7H6O4	5,51		153,01879	109,0281	108,0203	91,0175	81,0331	
3	Pantothenic acid	C9H17NO5	6,17	220,11850		202,1079	184,0978	174,1131	116,0346	90,0556
4	Neochlorogenic acid (5-O-Caffeoylquinic acid)	C16H18O9	10,22	355,10291		163,0391	145,0286	135,0444	117,0338	89,0390
5	Prodelphinidin C	C30H26O13	11,74		593,12952	425,0895	407,0777	289,0730	177,0184	125,0230
6	3-O-(4-Coumaroyl)quinic acid	C16H18O8	13,29		337,09235	191,0552	173,0444	163,0390	119,0489	93,0330
7[1]	Catechin	C15H14O6	14,00		289,07121	245,0818	205,0501	203,0708	125,0231	109,0281
8	Esculetin (6,7-Dihydroxycoumarin)	C9H6O4	14,71	179,03444		151,0394	133,0283	123,0444	105,0338	
9[1]	Chlorogenic acid (3-O-Caffeoylquinic acid)	C16H18O9	14,85	355,10291		163,0391	145,0286	135,0443	117,0339	89,0392
10	3-O-Feruloylquinic acid	C17H20O9	15,08		367,10291	193,0501	191,0558	173,0424	134,0361	
11	Caffeic acid	C9H8O4	15,14		179,03444	135,0439	107,0488			
12	Procyanidin B	C30H26O12	15,64		577,13460	451,1045	425,0883	407,0773	289,0722	125,0230
13	Cinchonain II isomer 1	C39H32O15	16,04		739,16630	587,1169	339,0519	289,0721	177,0186	
14	Chryptochlorogenic acid (4-O-Caffeoylquinic acid)	C16H18O9	16,11	355,10291		163,0391	145,0286	135,0443	117,0339	89,0391
15	Cinchonain II isomer 2	C39H32O15	16,99		739,16630	587,1225	339,0506	289,0719	177,0183	
16	2-Oxindole	C8H7NO	17,22	134,06059		106,0656	105,0340	79,0549		
17	Procyanidin C	C45H38O18	17,27		865,19799	695,1398	577,1353	407,0772	289,0722	125,0230
18	5-O-(4-Coumaroyl)quinic acid	C16H18O8	17,40		337,09235	191,0555	173,0438	163,0386	119,0487	93,0330
19[1]	Epicatechin	C15H14O6	17,55		289,07121	245,0818	205,0501	203,0709	125,0230	109,0281
20	Cinchonain II isomer 3	C39H32O15	17,86		739,16630	587,1193	339,0510	289,0723	177,0183	
21	Cinchonain II isomer 4	C39H32O15	18,04		739,16630	587,1184	339,0513	289,0721	177,0183	
22	4-O-(4-Coumaroyl)quinic acid	C16H18O8	18,06		337,09235	191,0556	173,0446	163,0391	119,0489	93,0331
23	Antiarol (3,4,5-Trimethoxyphenol)	C9H12O4	18,47	185,08139		170,0576	154,0626	153,0548	139,0393	125,0600
24[1]	4-Coumaric acid	C9H8O3	18,50		163,03952	119,0488	93,0331			
25	Tuberonic acid or 12-Hydroxyjasmonic acid	C12H18O4	18,74		225,11269	181,1237	165,0908	147,0801	135,0802	59,0123
26	4-O-Feruloylquinic acid	C17H20O9	18,98		367,10291	193,0495	191,0553	173,0445	134,0362	93,0329
27	Riboflavin	C17H20N4O6	19,07	377,14611		359,1358	243,0880	172,0874	99,0447	69,0344
28	Cinchonain I isomer 1	C24H20O9	19,30		451,10291	341,0669	289,0718	231,0295	217,0138	189,0187
29	Naringenin-C-hexoside isomer 1	C21H22O10	19,82	435,12913		399,1089	339,0872	315,0885	285,0753	195,0292

30[1]	Taxifolin (Dihydroquercetin)	C15H12O7	19,88		303,05048	285,0410	175,0389	153,0184	125,0230	57,0333
31	Quercetin-O-rhamnosyldihexoside	C33H40O21	20,26		771,19839	301,0357	300,0279	299,0204	271,0251	255,0299
32	Naringenin-C-hexoside isomer 2	C21H22O10	20,36	435,12913		399,1071	339,0875	315,0874	285,0755	195,0293
33	Quercetin-O-hexosylhexoside	C27H30O17	20,66		625,14048	301,0358	300,0278	299,0203	271,0250	255,0299
34	Naringenin-C-hexoside isomer 3	C21H22O10	20,71	435,12913		417,1194	369,0955	339,0853	219,0292	195,0292
35	Quercetin-O-dirhamnosylhexoside	C33H40O20	21,27		755,20347	301,0352	300,0277	299,0201	271,0252	255,0301
36	Hexahydroxy(iso)flavone-O-hexoside	C21H20O13	21,45		479,08257	317,0301	316,0229	287,0201	271,0250	
37	Hexahydroxy(iso)flavone-O-rhamnosylhexoside	C27H30O17	21,53		625,14048	317,0303	316,0226	315,0151	287,0202	271,0252
38	Cinchonain I isomer 2	C24H20O9	21,70		451,10291	341,0669	289,0720	231,0290	217,0137	189,0185
39[1]	Vitexin (Apigenin-8-C-glucoside)	C21H20O10	21,86	433,11348		415,1028	397,0926	367,0822	313,0710	283,0604
40	Tetrahydroxyxanthone isomer 1	C13H8O6	22,20		259,02427	231,0293	215,0343	203,0345	187,0382	
41	Cinchonain I isomer 3	C24H20O9	22,70		451,10291	341,0665	289,0720	231,0295	217,0137	189,0190
42	Isovitexin (Apigenin-6-C-glucoside)	C21H20O10	22,76	433,11348		415,1026	397,0922	337,0710	313,0709	283,0604
43	Luteolin-7-O-glucoside (Cynaroside)	C21H20O11	22,85		447,09274	327,0506	285,0408	284,0328	151,0026	133,0278
44[1]	Naringin (Naringenin-7-O-neohesperidoside)	C27H32O14	23,42		579,17139	459,1131	271,0615	151,0025	119,0489	
45[1]	Isoquercitrin (Quercetin-3-O-glucoside)	C21H20O12	23,44		463,08765	301,0357	300,0279	271,0251	255,0299	151,0026
46	Luteolin-7-O-rutinoside (Scolymoside)	C27H30O15	23,51		593,15065	447,0932	285,0410	284,0331	151,0020	133,0273
47[1]	Rutin (Quercetin-3-O-rutinoside)	C27H30O16	23,52	611,16122		465,1029	303,0503	129,0551	85,0291	71,0499
48	Kaempferol-3-O-rutinoside (Nicotiflorin)	C27H30O15	25,38		593,15065	327,0521	285,0408	284,0330	255,0298	227,0345
49	Cinchonain I isomer 4	C24H20O9	25,40		451,10291	341,0669	289,0723	231,0296	217,0138	189,0186
50[1]	Eriodictyol (3′,4′,5,7-Tetrahydroxyflavanone)	C15H12O6	25,45		287,05556	151,0026	135,0440	125,0229	107,0125	
51	Tetrahydroxy(iso)flavone-O-rhamnosylhexoside	C28H32O16	25,72		623,16122	315,0516	314,0427	300,0279	299,0205	271,0252
52	Abscisic acid	C15H20O4	25,84		263,12834	219,1386	204,1152	201,1282	152,0832	151,0752
53	Tetrahydroxyxanthone isomer 2	C13H8O6	26,76		259,02427	231,0303	215,0342	203,0347	187,0397	
54[1]	Quercetin (3,3',4',5,7-Pentahydroxyflavone)	C15H10O7	27,54		301,03483	273,0421	178,9979	151,0025	121,0282	107,0126
55[1]	Naringenin (4',5,7-Trihydroxyflavanone)	C15H12O5	27,76		271,06069	177,0183	165,0177	151,0026	119,0489	107,0125
56[1]	Luteolin (3',4',5,7-Tetrahydroxyflavone)	C15H10O6	28,40		285,03991	217,0503	175,0390	151,0025	149,0234	133,0282
57[1]	Apigenin (4',5,7-Trihydroxyflavone)	C15H10O5	30,26		269,04500	225,0536	201,0551	151,0031	149,0228	117,0334
58	Methoxy-trihydroxy(iso)flavone	C16H12O6	30,46		299,05556	284,0329	256,0374			

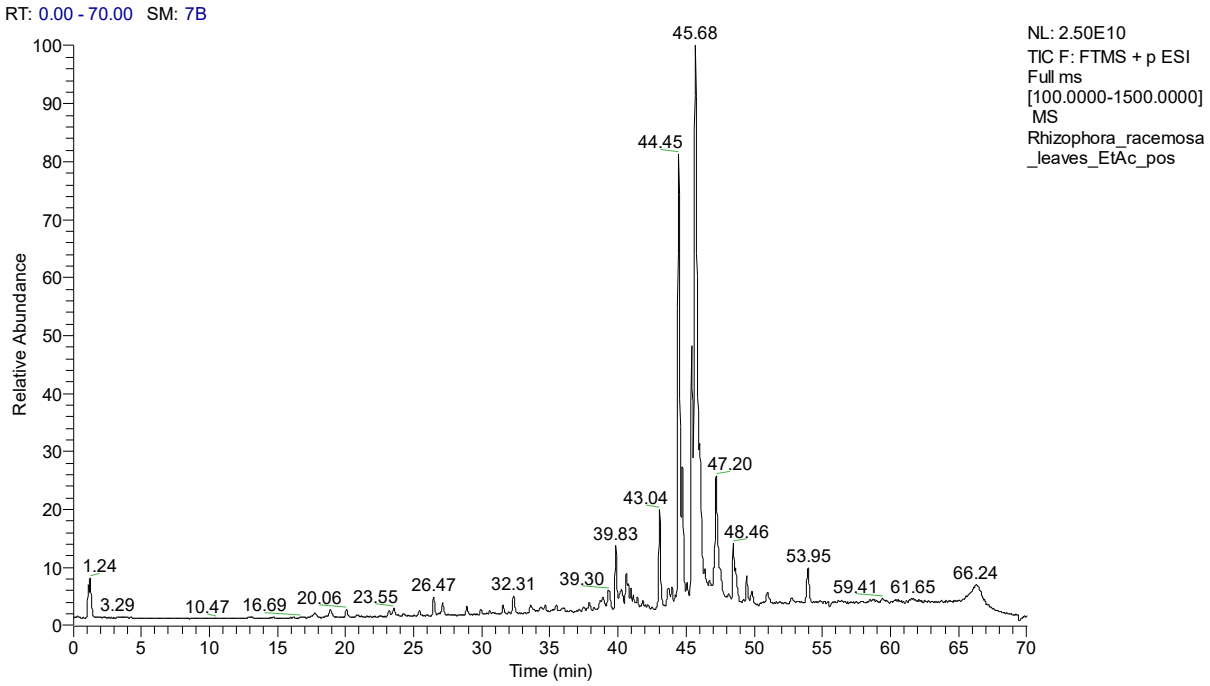


(a)

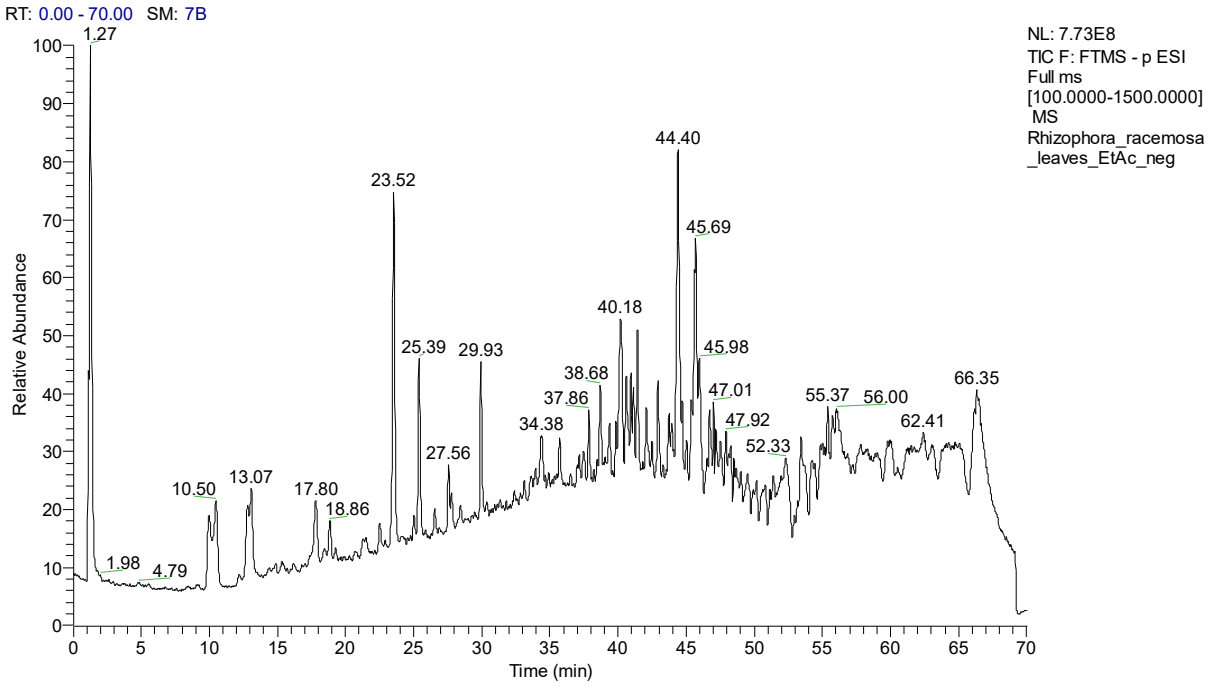


(b)

Figure S1. Total ion chromatograms of leaves infusion in positive (a) and negative (b) mode

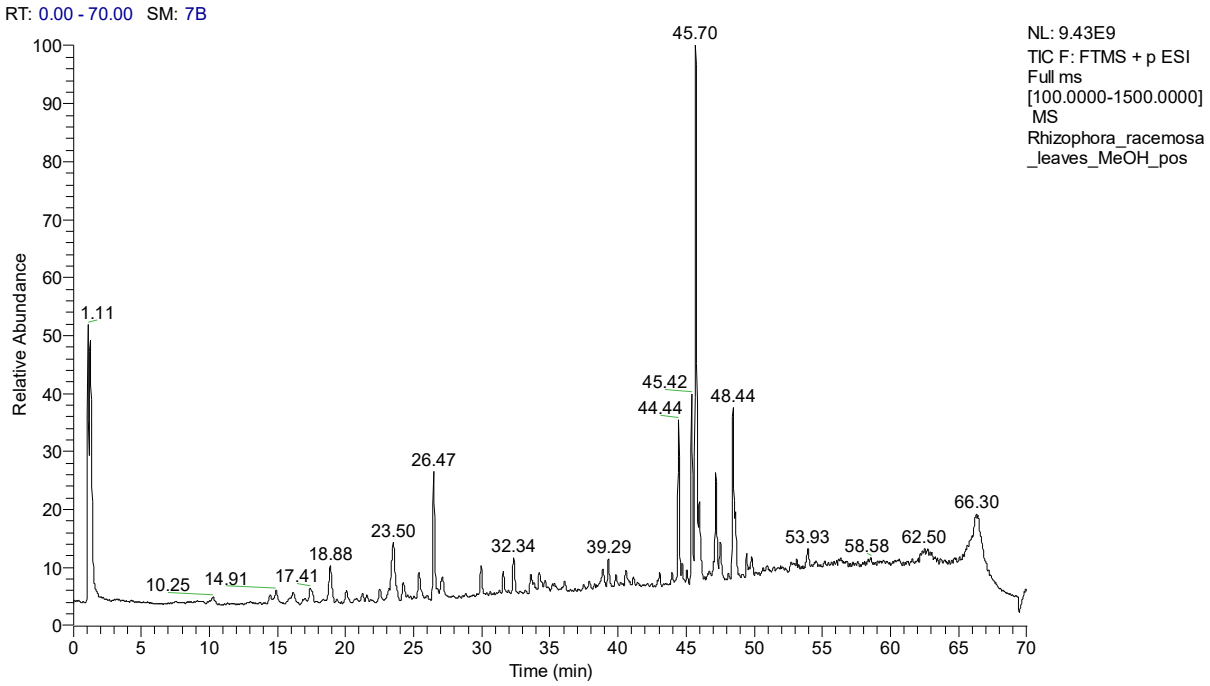


(a)

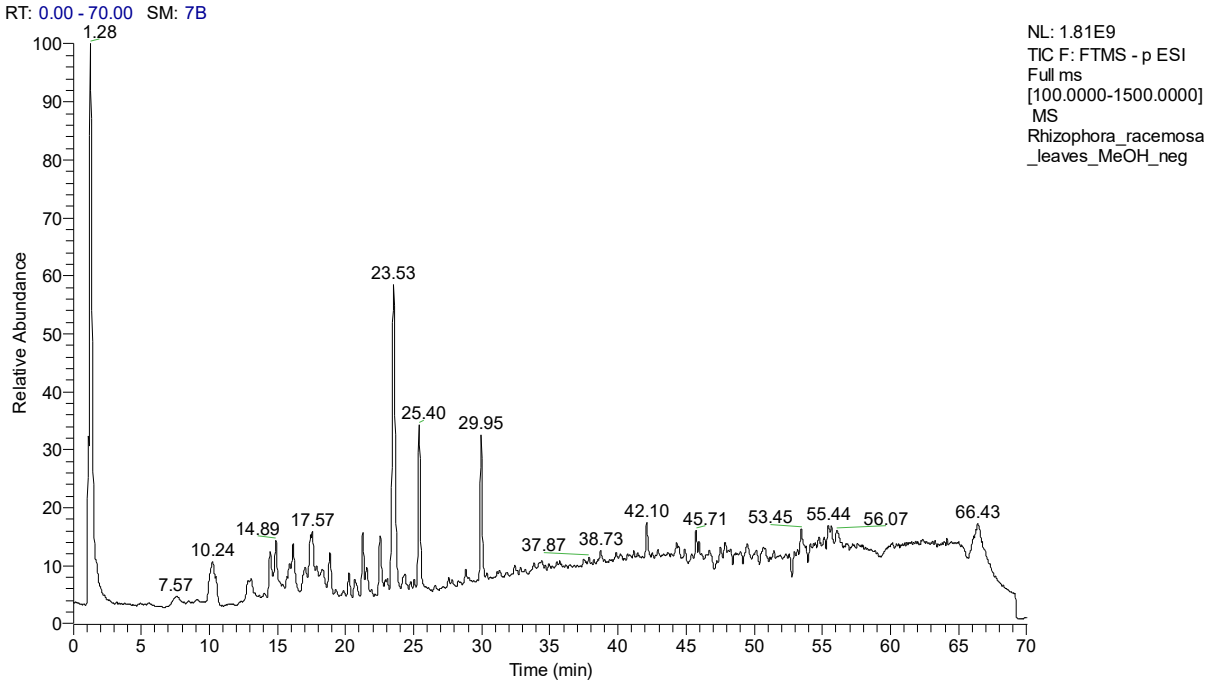


(b)

Figure S2. Total ion chromatograms of leaves ethyl acetate extract in positive (a) and negative (b) mode

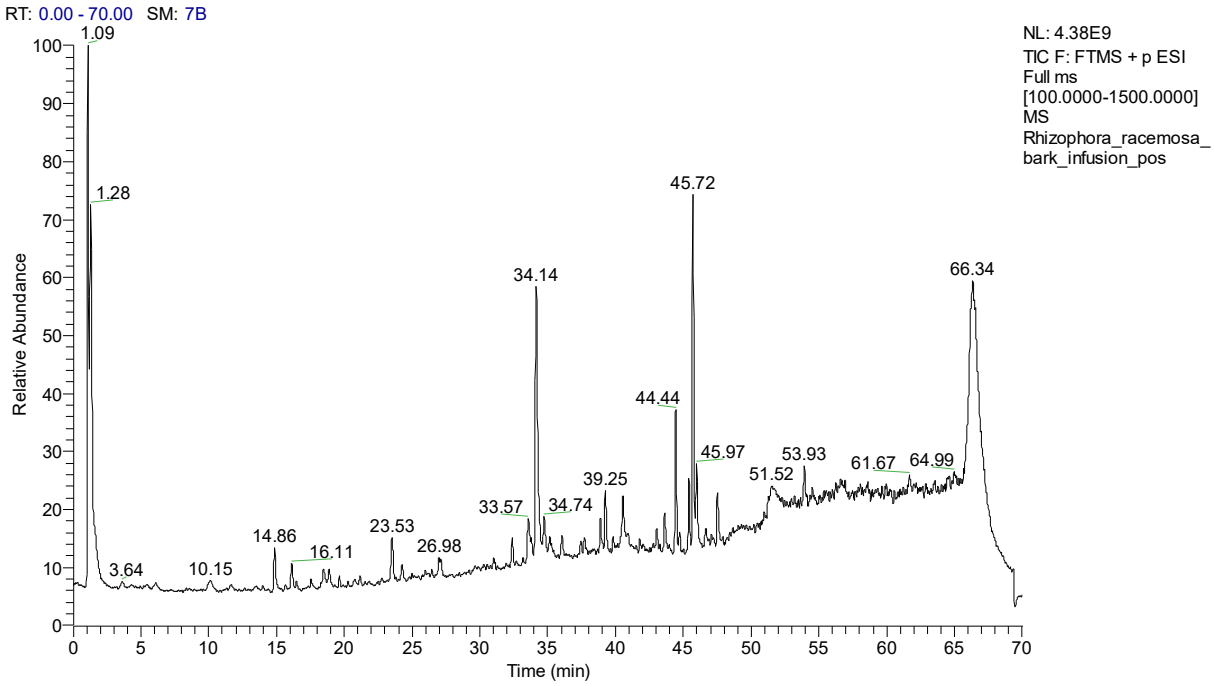


(a)

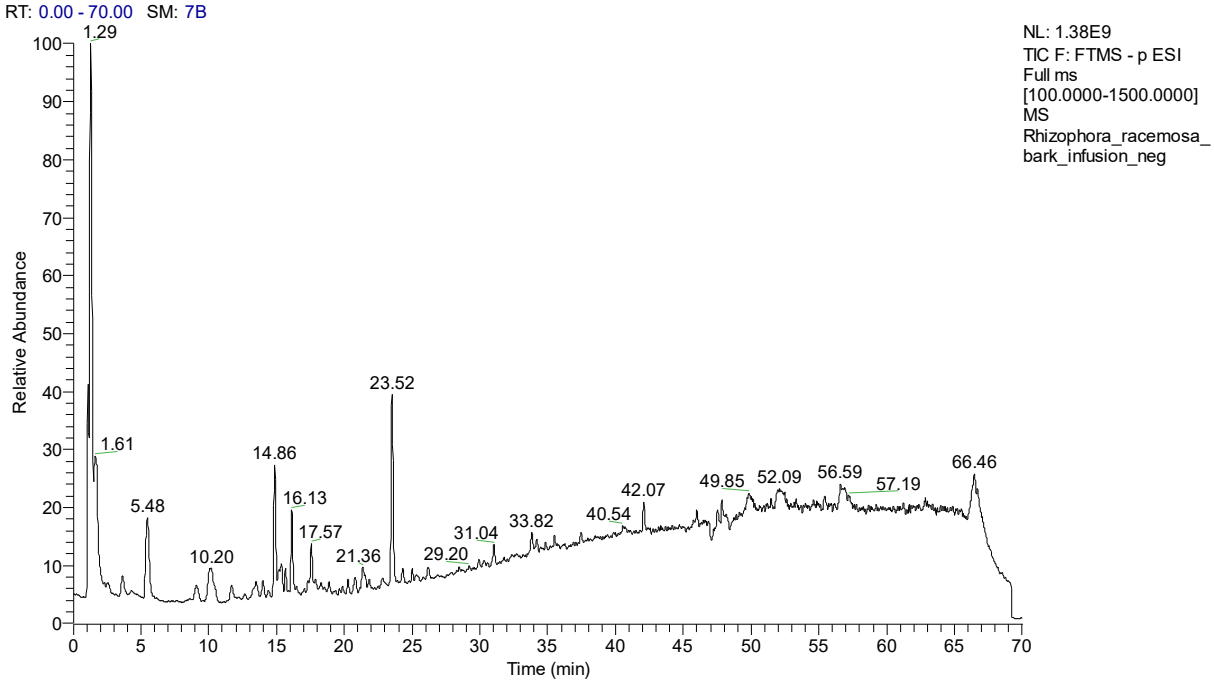


(b)

Figure S3. Total ion chromatograms of leaves methanol extract in positive (a) and negative (b) mode

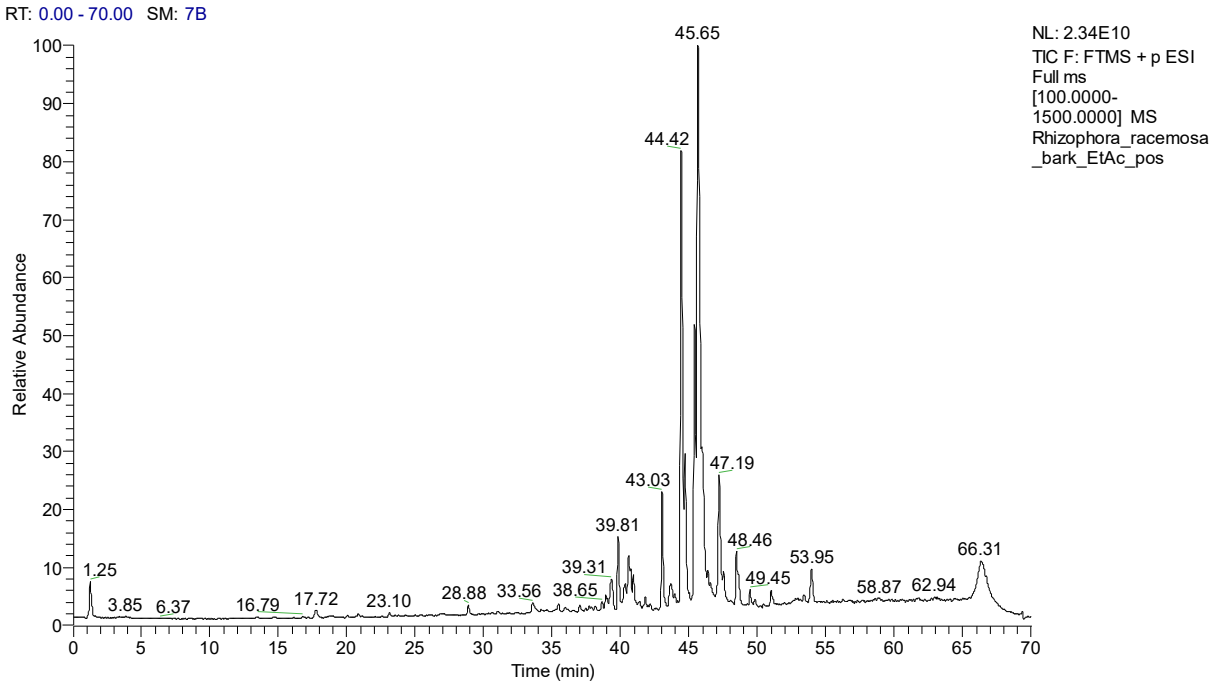


(a)



(b)

Figure S4. Total ion chromatograms of bark infusion in positive (a) and negative (b) mode



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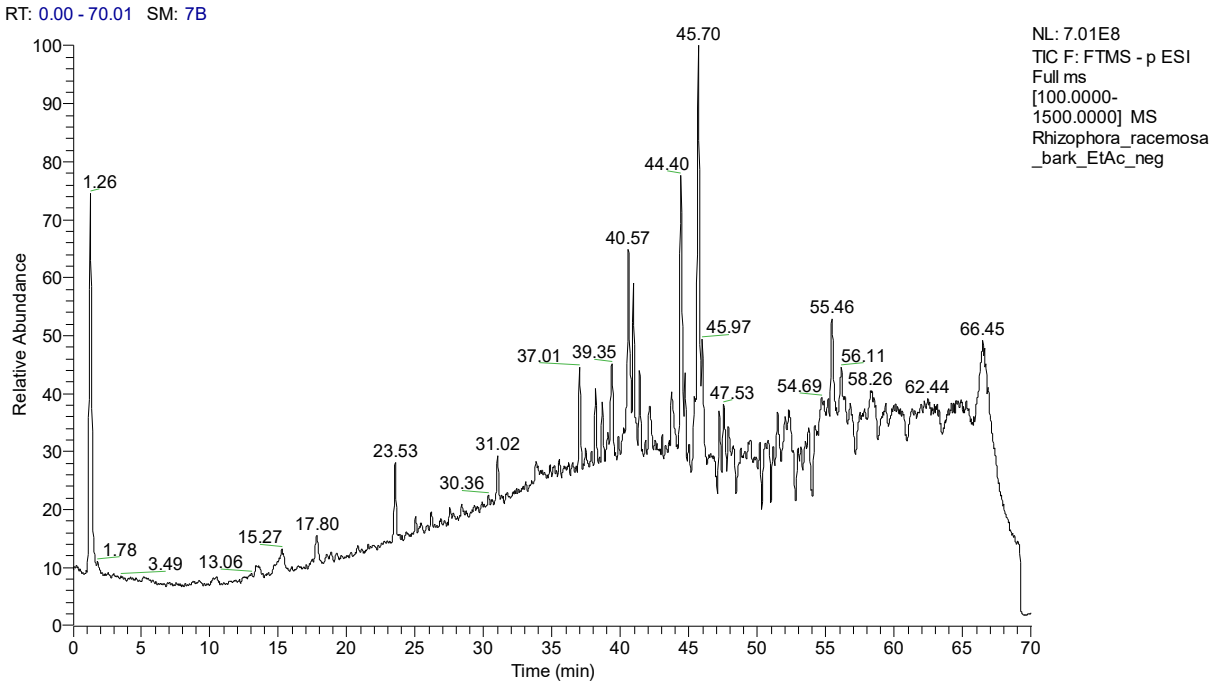
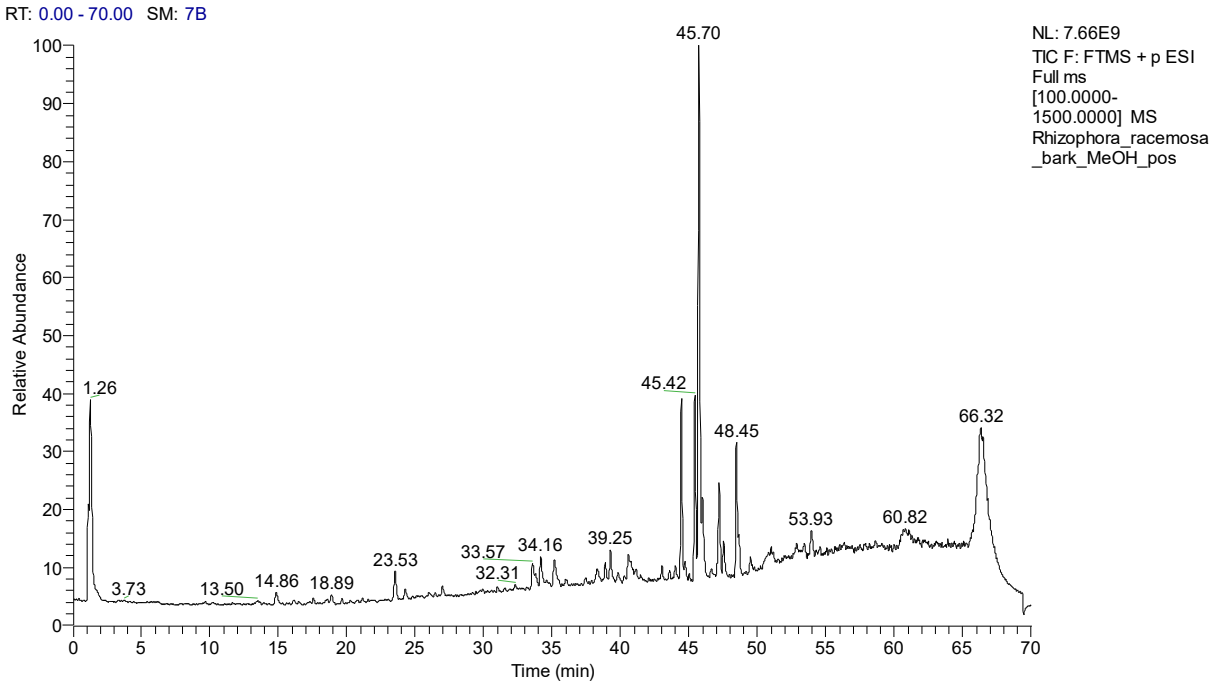
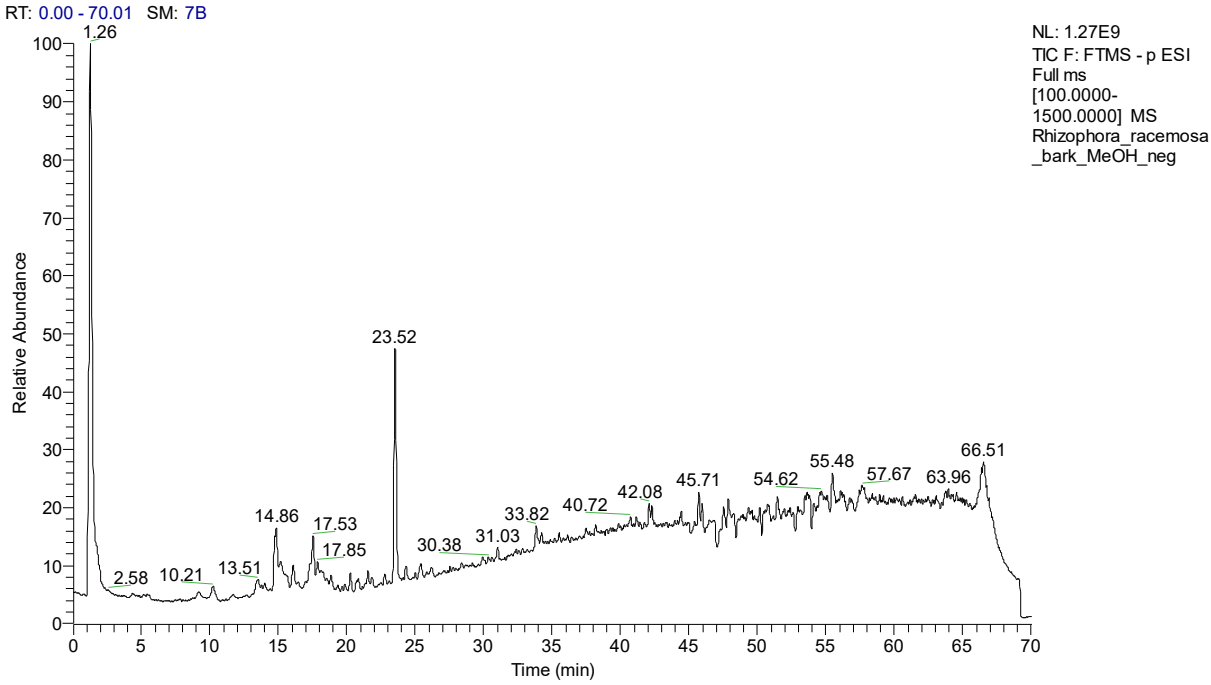


(b)

Figure S5. Total ion chromatograms of bark ethyl acetate in positive (a) and negative (b) mode



(a)



(b)

Figure S5. Total ion chromatograms of bark methanol in positive (a) and negative (b) mode

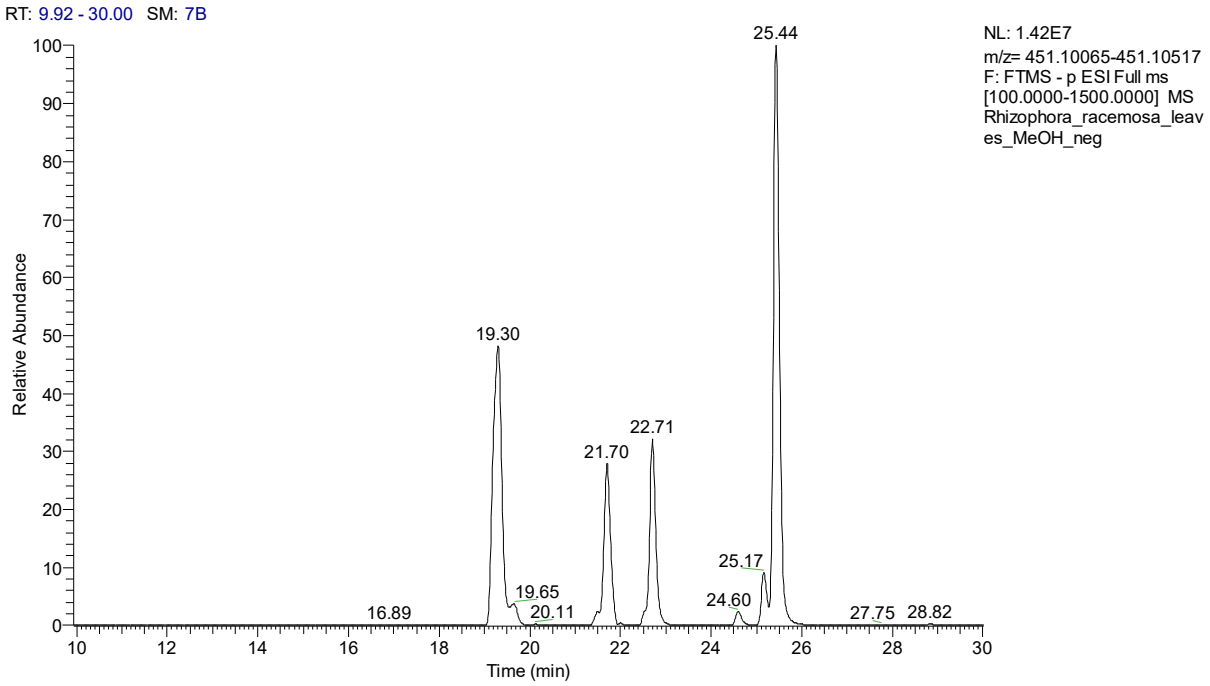


Figure S6. Extracted Ion Chromatogram (XIC) of Cinchonain I Isomers in Methanolic Extract of Leaves

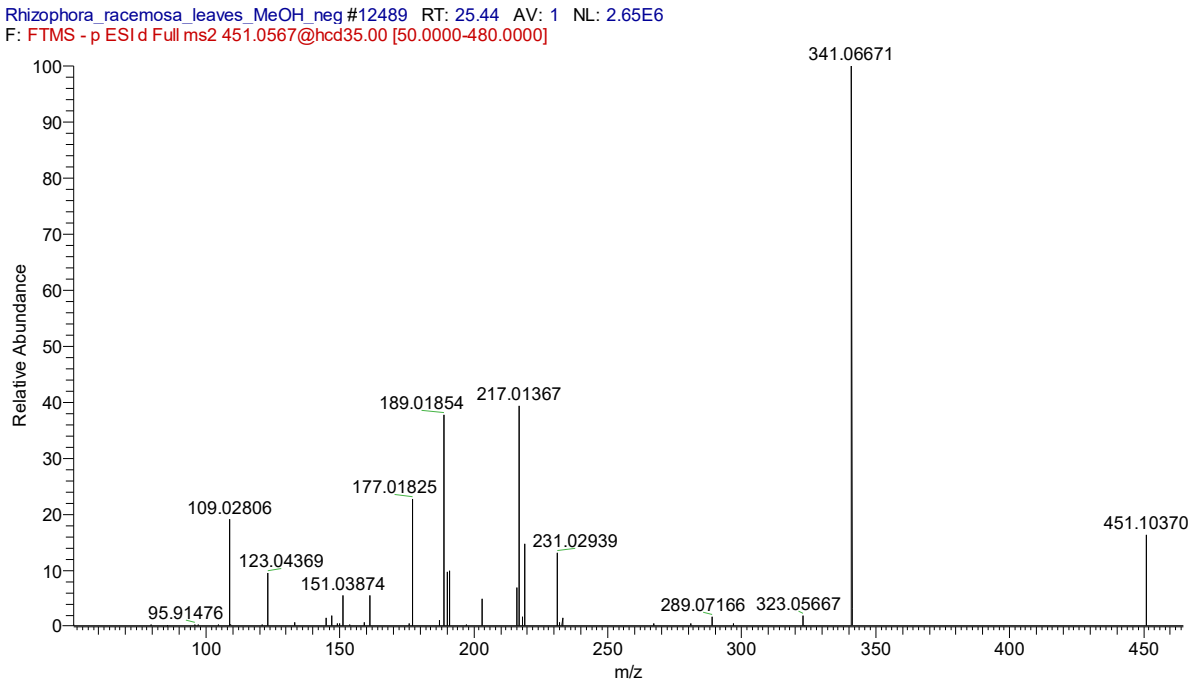


Figure S6. MS2 spectrum of Cinchonain I Isomer at Retention Time 25.44 minutes

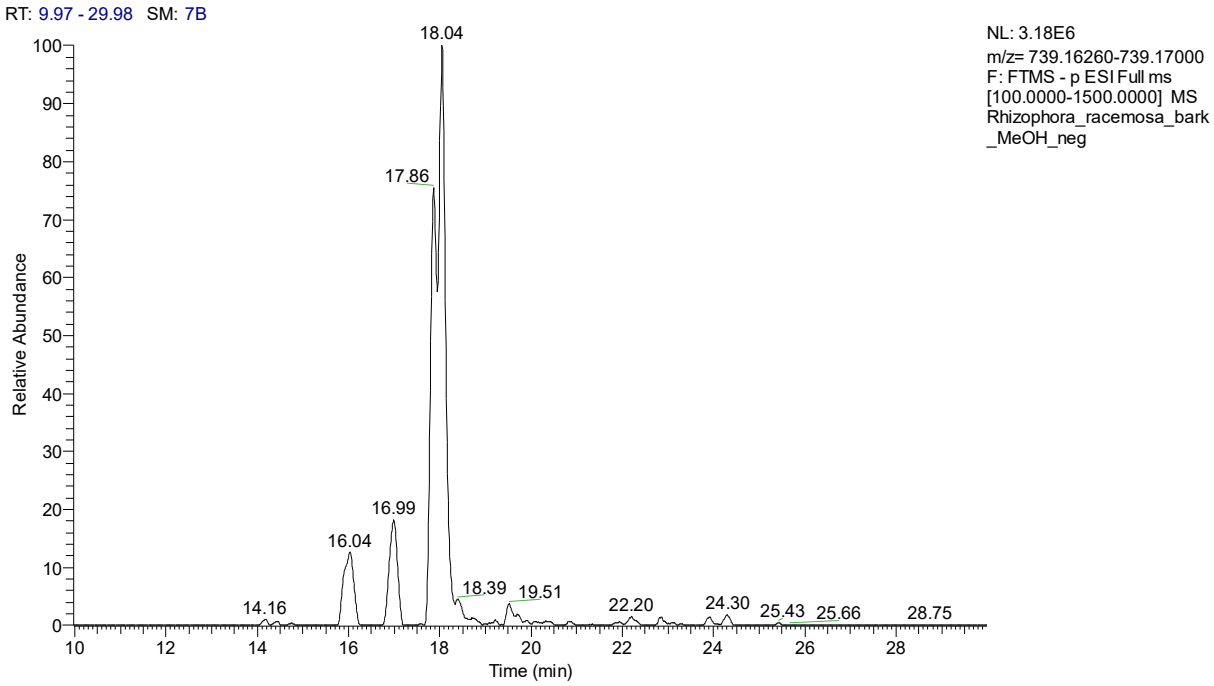


Figure S7. Extracted Ion Chromatogram (XIC) of Cinchonain II Isomers in Methanolic Extract of Bark

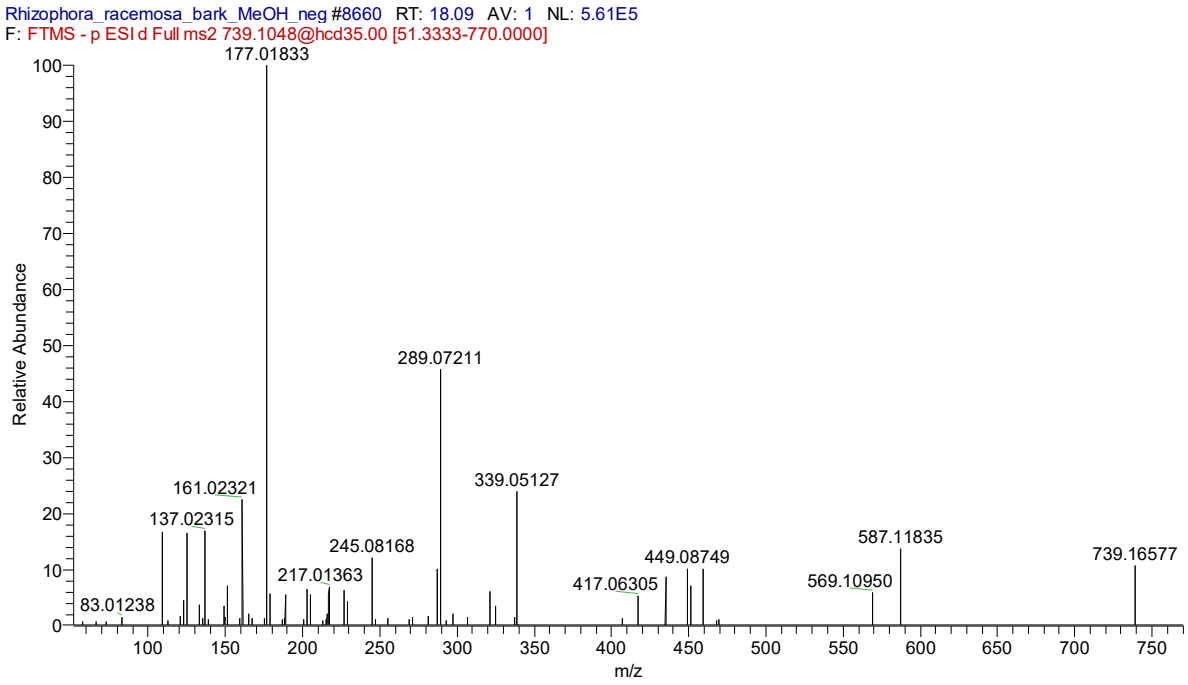


Figure S8. MS2 spectrum of Cinchonain II Isomer at Retention Time 18.04 minutes

References

1. Uysal, S.; Zengin, G.; Locatelli, M.; Bahadori, M. B.; Mocan, A.; Bellagamba, G.; De Luca, E.; Mollica, A.; Aktumsek, A., Cytotoxic and enzyme inhibitory potential of two Potentilla species (P. speciosa L. and P. reptans Willd.) and their chemical composition. *Frontiers in pharmacology* **2017,** 8, 290.
2. Grochowski, D. M.; Uysal, S.; Aktumsek, A.; Granica, S.; Zengin, G.; Ceylan, R.; Locatelli, M.; Tomczyk, M., In vitro enzyme inhibitory properties, antioxidant activities, and phytochemical profile of Potentilla thuringiaca. *Phytochemistry Letters* **2017,** 20, 365-372.