

Supplementary Materials

Figure S1. Scheme illustrating the process of sequential extraction and fractionation of the dried leaves of *Gaultheria procumbens* L.

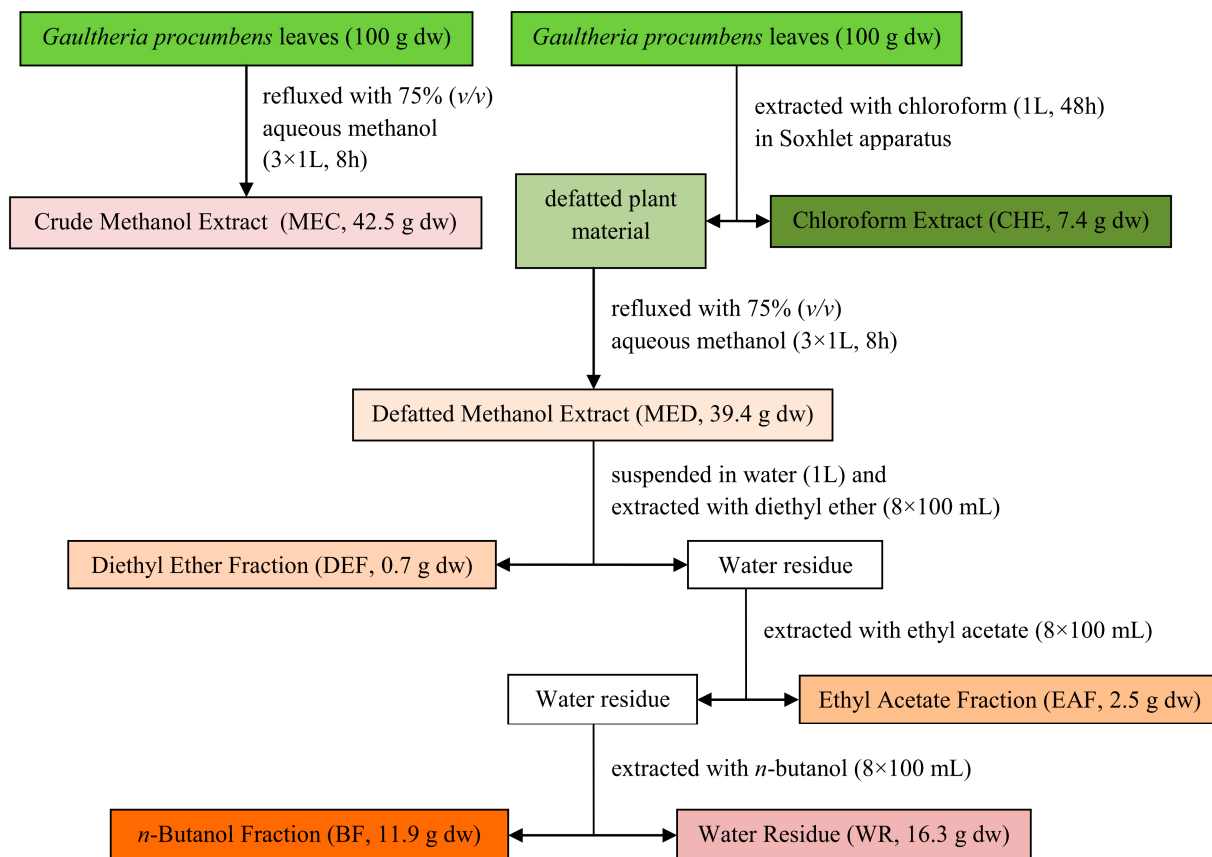


Table S1. Retention times, UV-Vis and MS³ data for compounds detected in the analyzed *Gaultheria* extracts.

	Compounds	Retention Time (min)	UV λ_{\max} (nm)	[M-H] ⁻ <i>m/z</i>	MS ² ions	MS ³ ions	[M+H] ⁺ <i>m/z</i>	MS ² ions	MS ³ ions
1	protocatechuic acid (PCA) ^a	4.4	295	153			155		
2	3- <i>O</i> -caffeoylquinic acid (neochlorogenic acid, NCHA) ^a	6.2	325	353	191, 179		377 ^b	359, 215	
3	<i>p</i> -hydroxybenzoic acid (<i>p</i> HBA) ^a	7.6	254	137	93		139		
4	3- <i>O</i> - <i>p</i> -coumaroylquinic acid ^a	9.3	310	337	163		339	147	
5	vanillic acid ^a	10.3	260, 291	167			169		
6	5- <i>O</i> -caffeoylquinic acid (chlorogenic acid, CHA) ^a	10.7	325	353	191, 179		377 ^b	359, 215	
7	(+)-catechin (CA) ^a	10.9	280	289	245, 205		291	165, 139, 123	
8	caffeic acid (CFA) ^a	11.7	325	179	135		181		
9	4- <i>O</i> -caffeoylquinic acid (cryptochlorogenic acid, CCHA) ^a	12.6	325	353	173		377 ^b	359, 215	
10	3- <i>O</i> -feruloylquinic acid	14.2	325	367	193		369	163	
11	procyanidin B-type dimer	14.9	280	577	425, 407, 289	407, 273	579	427, 409, 291	409, 301, 275
12	unknown compound	15.7	254	481	385, 345, 327, 165, 153		483		
13	(-)-epicatechin (ECA) ^a	16.5	280	289	245, 205		291	165, 139, 123	
14	4- <i>O</i> - <i>p</i> -coumaroylquinic acid	16.6	310	337	173		339		
15	unknown compound	17.3	280	559	542, 445, 407, 293, 265		561	295, 259, 153	
16	<i>p</i> -coumaric acid (<i>p</i> CA) ^a	19.1	310	163	119		165		
17	procyanidin A-type trimer (PA)	19.8	280	863	711, 693, 573, 559, 451, 411, 289	693, 559, 407, 285	865	713, 695, 575, 533, 453, 411, 287	695, 543, 409, 287
18	procyanidin B-type trimer	20.8	280	865	713, 695, 577, 407, 287	695, 561, 407, 245	867	715, 699, 579, 427, 407, 287,	697, 545, 425, 245
19	procyanidin A-type dimer	22.1	280	575	499, 423, 407, 289		577	492, 407, 289, 165	
20	unknown compound	22.2	267, 298	639	319, 183	183, 165, 153	641		
21	caffeoylquinic acid derivative	22.4	325	391	179		393		

Table S1. Cont.

	Compounds	Retention Time (min)	UV λ_{\max} (nm)	[M-H] ⁻ <i>m/z</i>	MS ² ions	MS ³ ions	[M+H] ⁺ <i>m/z</i>	MS ² ions	MS ³ ions
22	unknown compound	24.3	280	473	427, 293		475	457, 431, 249, 166	
23	quercetin pentoside-glucuronide	24.9	257, 356	609	482, 301	301	611	479, 303	303
24	procyanidin A-type trimer	25.1	280	863	711, 573, 559, 451, 411	693, 559, 542, 407	865	713, 533, 407, 287	695, 543, 409, 287
25	unknown compound	26.3	280	451	341		453	343, 301, 191	191
26	quercetin 3- <i>O</i> -galactoside (hyperoside, HY) ^a	27.2	254, 353	463	301	271, 255, 179, 151	465	303	285, 257, 229, 165
27	quercetin 3- <i>O</i> -glucoside (isoquercitrin, IQ) ^a	28.1	256, 353	463	301	271, 255, 179, 151	465	303	285, 257, 229, 165
28	quercetin 3- <i>O</i> -glucuronide (miquelianin, MQ) ^a	28.8	256, 356	477	301	273, 257, 179, 151	479	303	285, 257, 229, 165
29	quercetin 3- <i>O</i> -arabinoside (guajiverin, GV) ^a	30.3	258, 356	433	301	271, 255, 229, 179, 151	435	303	285, 257, 229, 165
30	quercetin derivative	30.6	258, 354	333	301, 165	165	335	303, 137	
31	kaempferol 3- <i>O</i> -glucuronide	33.0	265, 349	461	285	257, 229, 163, 151	463	287	259, 231, 213, 165, 153
32	quercetin 3- <i>O</i> -glucuronide methyl ester	33.9	265, 356	491	473, 315, 301	301	493	303	
33	kaempferol 3- <i>O</i> -glucuronide methyl ester	38.8	265, 348	475	327, 285, 255		477	287	
34	unknown compound	39.0	286, 326	409	335, 235, 161		411	393, 249, 163	
35	kaempferol 3- <i>O</i> -glucoside (astragalol, AG) ^a	39.9	265, 345	447	285		449	287	231, 213, 165
36	unknown compound	40.3	280	451	341, 217		453	343, 301	191
37	quercetin (QU) ^a	43.3	255, 364	301	273, 257, 229, 179, 159		303	285, 257, 229, 165	
38	unknown compound	43.7	286, 326	409	335, 235, 179, 161, 135		411	393, 249, 163	
39	unknown compound	44.4	280	435	341, 297		437	343, 285, 191	191
40	quercetin 3- <i>O</i> -pentoside-glucuronide butyl ester	46.8	268, 359	665	647, 533, 357, 301	515, 357, 301, 178	667	535, 303, 215	303, 215
41	quercetin 3- <i>O</i> -glucuronide butyl ester	48.8	256, 356	533	515, 357, 301, 179	301	535	303	
42	kaempferol 3- <i>O</i> -pentoside-glucuronide butyl ester	50.1	268, 350	649	631, 533, 499, 285, 255		651	519, 287, 215	287
43	kaempferol (KA) ^a	50.4	265, 364	285			287		
44	kaempferol 3- <i>O</i> -glucuronide butyl ester	50.6	265, 350	517	285, 255		519	287	

Notes: ^a comparisons with authentic standard have been made; ^b [M+Na]⁺; in bold—ions subjected to MS³ fragmentation.