

Article

The Effect of Standardised Leaf Extracts of *Gaultheria procumbens* on Multiple Oxidants, Inflammation-Related Enzymes, and Pro-Oxidant and Pro-Inflammatory Functions of Human Neutrophils

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Supplementary Materials:

Table S1. Phenolic analytes detected in *G. procumbens* leaf dry extracts by UHPLC-PDA-ESI-MS³.

Table S2. Correlation (*r*) coefficients and probability (*p*) values of linear relationships between antioxidant and anti-inflammatory activity parameters and phenolic contents of *G. procumbens* leaf dry extracts.

Table S1. Phenolic analytes detected in *G. procumbens* leaf dry extracts by UHPLC-PDA-ESI-MS³.

Peak	Analyte	t _R (min)	UV λ _{max} (nm)	[M–H] [–] m/z	MS ² (% relative abundance)	MS ³ (% relative abundance)	Extract
1	protocatechuic acid hexoside	4.1	259, 293	315	225 (25); 153 (100); 107 (8)		All
2	protocatechuic acid ^a	4.6	259, 293	153			All
3	protocatechuic acid hexoside	5.6	259, 293	315	225 (1); 153 (100); 107 (2)		ME
4	unknown compound	5.8	310	331	313 (100); 211 (9); 167 (42); 125 (9)		All
5	3- <i>O</i> -caffeoylquinic acid (neochlorogenic acid) ^a	6.4	325	353	191 (100); 179 (50)		All
6	3- <i>O</i> - <i>p</i> -coumaroylquinic acid derivative	6.8	310	371	353 (6); 325 (72); 163 (100)		All
7	<i>p</i> -hydroxybenzoic acid ^a	7.6	254	137			EAE
8	procyanidin A-type dimer	9.4	280	575	499 (100); 490 (84); 451 (22); 407 (17); 289 (7)		All
9	3- <i>O</i> - <i>p</i> -coumaroylquinic acid hexoside	10.3	310	325	163 (100); 119 (9)		All
10	5- <i>O</i> -caffeoylquinic acid (chlorogenic acid) ^a	11.0	325	353	191 (100); 179 (5)		All
11	methyl salicylate 2- <i>O</i> -β-D-glucopyranosyl-(1→2)-[<i>O</i> -β-D-xylopyranosyl-(1→6)]- <i>O</i> -β-D-glucopyranoside ^{a, b}	12.6	285	653 *	607 (100); 575 (12)		ME, BE
12	4- <i>O</i> -caffeoylquinic acid (cryptochlorogenic acid) ^a	12.8	325	353	173 (100)		ME, BE
13	procyanidin B-type dimer	14.0	280	577	559 (17); 451 (41); 425 (100) ; 407 (44); 289 (27)	407 (100); 339 (2); 273 (7)	All
14	procyanidin B2 ^a	15.2	280	577	425 (100) ; 407 (51); 289 (15)	407 (100); 273 (6)	ME, BE
15	procyanidin B-type trimer	15.5	280	865	847 (15); 739 (79); 713 (48) ; 695 (67); 577 (79); 451 (21); 287 (38)	695 (100); 575 (45); 561 (11); 425 (21); 405 (34); 287 (16)	All
16	gaultherin isomer ^b	15.7	285	491 *	445 (7); 413 (10); 293 (100); 149 (4)		All
17	unknown compound	16.2	280	417	373 (100); 331 (75)		ME, BE
18	(–)-epicatechin ^a	16.5	280	289	245 (100); 205 (19)		All
19	caffeoylquinic acid derivative	16.9	325	431	385 (100); 277 (7); 179 (22)		ME, BE
20	gaultherin ^a	17.1	285	491 *	445 (7); 413 (4); 293 (100); 149 (2)		All
21	unknown compound	17.7	280	363	345 (4); 183 (100); 179 (19); 143 (7); 121 (14)		All

Table S1. Cont.

Peak	Analyte	t _R (min)	UV λ_{max} (nm)	[M-H] ⁻ m/z	MS ² (% relative abundance)	MS ³ (% relative abundance)	Extract
22	procyanidin A-type trimer	18.4	280	863	711 (100) ; 573 (32); 559 (19); 451 (53); 411 (75); 289 (100)	693 (100); 559 (49); 541 (9); 407 (11)	ME, BE
23	procyanidin B-type dimer	19.3	280	577	559 (11); 451 (38); 425 (100) ; 407 (46); 289 (36)	407 (100); 381 (13); 299 (18); 273 (4)	All
24	procyanidin A-type trimer (cinnamtannin B-1) ^{a, b}	20.0	280	863	711 (100) ; 693 (11); 573 (23); 559 (15); 451 (16); 411 (13); 289 (5)	693 (79); 559 (100); 541 (33); 463 (14); 407 (26)	All
25	procyanidin B-type trimer (procyanidin C1) ^{a, b}	21.2	280	865	847 (36); 739 (71); 713 (45) ; 695 (100); 577 (95); 451 (19); 287 (20)	693 (100); 561 (64); 411 (19); 243 (4)	ME, BE
26	procyanidin A-type trimer	21.6	280	863	711 (100) ; 573 (41); 559 (10); 451 (53); 411 (78); 289 (25)	693 (100); 559 (79); 541 (28); 463 (19); 407 (21)	ME, BE
27	caffeoylquinic acid derivative	22.2	325	391	225 (17); 179 (100); 161 (4); 143 (9); 119 (7); 113 (6)		All
28	procyanidin A-type dimer	22.4	280	575	499 (100); 491 (4); 451 (8); 423 (16); 289 (22)		All
29	procyanidin A-type dimer	23.4	280	575	499 (100); 491 (67); 451 (11); 423 (24); 289 (73)		ME, BE
30	procyanidin A-type dimer	24.7	280	575	499 (100); 491 (21); 451 (13); 423 (18); 289 (37)		All
31	quercetin 3-O- β -D-xylopyranosyl-(1 \rightarrow 2)- β -D-glucuronopyranoside (wintergreenoside A) ^{a, b}	25.5	257, 356	609	477 (2); 301 (100)	273 (47); 255 (17); 179 (100); 151 (79)	ME, BE
32	procyanidin A-type dimer	26.4	280	575	499 (23); 491 (16); 451 (6); 411 (57); 289 (100)		ME, BE
33	procyanidin A-type trimer	26.8	280	863	711 (100) ; 573 (58); 559 (9); 451 (58); 411 (87); 289 (29)	693 (100); 559 (11); 541 (15); 463 (42); 407 (28)	All
34	3-O-p-coumaroylquinic acid derivative	27.2	310	487	441 (100); 307 (73); 163 (7)		ME, EAE
35	quercetin 3-O- β -D-galactopyranoside (hyperoside) ^a	27.6	254, 353	463	301 (100)	273 (49); 255 (19); 179 (95); 151 (75)	All
36	quercetin 3-O- β -D-glucopyranoside (isoquercitrin) ^a	28.5	256, 353	463	301 (100)	273 (53); 255 (25); 179 (100); 151 (71)	All
37	quercetin 3-O- β -D-glucuronopyranoside (miquelianin) ^a	29.1	256, 356	477	301 (100)	273 (17); 257 (16); 179 (100); 151 (61)	All

Table S1. Cont.

Peak	Analyte	t _R (min)	UV λ _{max} (nm)	[M-H] ⁻ m/z	MS ² (% relative abundance)	MS ³ (% relative abundance)	Extract
38	kaempferol 3-O-β-D-xylopyranosyl-(1→2)-β-D-glucuronopyranoside (wintergreenoside B) ^{a, b}	29.4	275, 345	593	285 (100)	267 (31); 257 (100); 241 (19); 229 (35); 151 (19)	ME, BE
39	quercetin 3-O-α-L-arabinopyranoside (guajjaverin) ^a	30.8	258, 356	433	301 (100)	273 (45); 255 (17); 179 (100); 151 (73)	All
40	kaempferol 3-O-β-D-glucuronopyranoside ^a	33.3	265, 345	461	285 (100)	267 (39); 257 (100); 241 (40); 229 (31); 151 (9)	ME, BE
41	quercetin ^a	43.7	255, 364	301	273 (41); 255 (18); 179 (100); 151 (74)		All

^a confirmed by comparison with authentic standard; ^b detected for the first time in *G. procumbens* leaf; t_R, retention times; UV λ_{max}, absorbance maxima in PDA spectra; [M-H]⁻, pseudomolecular ions in MS spectra recorded in a negative ion mode; in bold – ions subjected to MS³ fragmentation; * [M+HCOO]⁻. The nomenclature of caffeoylquinic acids isomers is according to IUPAC.

Table S2. Correlation (*r*) coefficients and probability (*p*) values of linear relationships between antioxidant and anti-inflammatory activity parameters and phenolic contents of *G. procumbens* leaf dry extracts.

<i>r</i> (<i>p</i>) for:	Antioxidant activity					Anti-inflammatory activity			
	DPPH	FRAP	TBARS	O ₂ ^{•−}	•OH	H ₂ O ₂	HYAL	LOX	COX-2
TPC	−0.6961 (0.510)	0.9841 (0.114)	−0.7996 (0.410)	−0.7459 (0.464)	−0.7302 (0.479)	−0.5171 (0.654)	−0.3675 (0.760)	−0.3351 (0.782)	−0.8080 (0.401)
TPH	0.9447 (0.213)	−0.5767 (0.609)	0.8820 (0.312)	−0.2889 (0.813)	0.9276 (0.244)	0.9942 (0.068)	0.9982 (0.038) *	0.9956 (0.060)	0.8753 (0.321)
TPA	−0.8892 (0.302)	0.9892 (0.094)	−0.9497 (0.203)	−0.4935 (0.671)	−0.9104 (0.271)	−0.7638 (0.447)	−0.6458 (0.553)	−0.6190 (0.575)	−0.9540 (0.194)
TLPA	−0.9841 (0.114)	0.9032 (0.282)	−0.9998 (0.014) *	−0.2178 (0.860)	−0.9916 (0.083)	−0.9191 (0.258)	−0.8407 (0.364)	−0.8215 (0.386)	−1.0000 (0.005) **
TPHA	0.8973 (0.291)	−0.4719 (0.687)	0.8174 (0.391)	−0.4043 (0.735)	0.8747 (0.322)	0.9735 (0.147)	0.9980 (0.040) *	0.9996 (0.018) *	0.8092 (0.400)
TSAL	0.9985 (0.035) *	−0.7795 (0.431)	0.9777 (0.135)	−0.0138 (0.991)	0.9947 (0.066)	0.9853 (0.109)	0.9431 (0.216)	0.9311 (0.238)	0.9747 (0.144)
TFL	−0.7831 (0.427)	0.9988 (0.031)	−0.8705 (0.328)	−0.6535 (0.547)	−0.8124 (0.396)	−0.6234 (0.571)	−0.4847 (0.678)	−0.4541 (0.700)	−0.8774 (0.319)

TPC: total phenolic content (Folin-Ciocalteu assay) in gallic acid equivalents, TPH: total phenolic content (HPLC), TSAL: total content of salicylates (HPLC), TPA: total content of proanthocyanidins (*n*-butanol/HCl assay) in cyanidin chloride equivalents, TLPA: total content of proanthocyanidins (HPLC), TPHA: total content of phenolic acids (HPLC), TFL: total content of flavonoids (HPLC). Asterisks mean significance of the estimated linear relationship (**p* < 0.05, ***p* < 0.01) for three extracts (*n* = 3).