

# Cellular Antioxidant Effect of an Aronia Extract and Its Polyphenolic Fractions Enriched in Proanthocyanidins, Phenolic Acids, and Anthocyanins

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**Table S1.** Polyphenol composition of aronia extract and its fractions determined by UPLC-UV-QToF. Values are expressed in mg/g of extract or fraction  $\pm$  standard deviation.

	Concentration (mg/g) (Mean $\pm$ Standard Deviation)			
	Aronia Extract	A1 Fraction	A2 Fraction	A3 Fraction
Catechin	0.140 $\pm$ 0.004	0.325 $\pm$ 0.011	0.736 $\pm$ 0.008	ND
Epicatechin	1.25 $\pm$ 0.04	2.10 $\pm$ 0.03	4.31 $\pm$ 0.10	0.81 $\pm$ 0.02
Flavan-3-ols monomers total	1.39 $\pm$ 0.04	2.42 $\pm$ 0.04	5.05 $\pm$ 0.10	0.81 $\pm$ 0.02
Procyanidin B2	2.213 $\pm$ 0.010	3.80 $\pm$ 0.02	1.50 $\pm$ 0.04	0.111 $\pm$ 0.010
Neochlorogenic acid	53.2 $\pm$ 0.2	108.4 $\pm$ 0.4	0.221 $\pm$ 0.006	0.138 $\pm$ 0.001
Chlorogenic acid	53.7 $\pm$ 0.2	111.2 $\pm$ 0.4	0.154 $\pm$ 0.004	0.125 $\pm$ 0.001
Cryptochlorogenic acid	4.624 $\pm$ 0.014	9.20 $\pm$ 0.05	ND	ND
Caffeoyl quinide	1.122 $\pm$ 0.013	2.03 $\pm$ 0.03	0.205 $\pm$ 0.002	ND
Coumaroyl quinic acid	1.582 $\pm$ 0.005	3.116 $\pm$ 0.015	ND	ND
Vanilloyl hexose	0.253 $\pm$ 0.008	0.566 $\pm$ 0.013	ND	ND
3,4-dihydroxybenzoic acid	0.121 $\pm$ 0.001	0.299 $\pm$ 0.003	ND	ND
<b>Phenolic acids total</b>	<b>114.6 <math>\pm</math> 0.5</b>	<b>234.9 <math>\pm</math> 1.0</b>	<b>0.580 <math>\pm</math> 0.011</b>	<b>0.263 <math>\pm</math> 0.002</b>
Quercetin-pentoside-hexoside	2.579 $\pm$ 0.002	5.01 $\pm$ 0.03	0.049 $\pm$ 0.001	ND
Quercetin hexoside deoxyhexoside 1	2.390 $\pm$ 0.008	4.77 $\pm$ 0.02	ND	ND
Quercetin-3-galactoside	3.978 $\pm$ 0.013	8.08 $\pm$ 0.04	0.049 $\pm$ 0.001	ND
Quercetin-3-rutinoside (Rutin)	2.291 $\pm$ 0.007	4.56 $\pm$ 0.02	ND	ND
Quercetin-3-glucoside	2.964 $\pm$ 0.009	5.98 $\pm$ 0.03	ND	ND
Quercetin-dihexoside 1	1.687 $\pm$ 0.004	3.287 $\pm$ 0.013	ND	ND
Quercetin-dihexoside 2	0.698 $\pm$ 0.002	1.470 $\pm$ 0.007	ND	ND
Quercetin	0.693 $\pm$ 0.004	1.76 $\pm$ 0.04	0.066 $\pm$ 0.001	ND
Quercetin-hexoside-deoxyhexoside 2	0.210 $\pm$ 0.001	0.407 $\pm$ 0.003	ND	ND
Quercetin-pentoside	0.194 $\pm$ 0.001	0.392 $\pm$ 0.002	ND	ND
Isorhametin-hexoside-deoxyhexoside 1	0.254 $\pm$ 0.004	0.512 $\pm$ 0.007	ND	ND
Isorhametin-hexoside-deoxyhexoside 2	0.233 $\pm$ 0.003	0.491 $\pm$ 0.002	ND	ND
<b>Flavonols total</b>	<b>18.17 <math>\pm</math> 0.05</b>	<b>36.7 <math>\pm</math> 0.2</b>	<b>0.165 <math>\pm</math> 0.002</b>	<b>ND</b>

**Table S2.** Identification of the polyphenolic compounds by UPLC-UV-QToF in aronia extract and its fractions.

Polyphenol class	Identification	RT (min)	[M-H] <sup>-</sup>	Molecular formula	Error (ppm)	MS2 Fragments (Relative Intensity)	Level *
Flavan-3-ols and PACs	Catechin	7.39	289.0711	C15H14O6	-0.35	203.0706 (100); 245.0814 (57)	1
	Epicatechin	10.81	289.0715	C15H14O6	1.04	245.0814 (100)	1
	Procyanidin B2	9.52	577.1348	C30H26O12	0.35	289.0717 (100); 407.0768 (87); 425.0872 (30); 245.0814 (23)	1
Phenolic acids	Neochlorogenic acid	5.06	353.0873	C16H18O9	0.73	191.0555 (100); 135.0447 (89); 179.0332 (57)	1
	Chlorogenic acid	8.08	353.0871	C16H18O9	-0.96	191.0561 (100)	1
	Cryptochlorogenic acid	8.90	353.0870	C16H18O9	-1.80	135.0451 (100); 173.0455 (67); 179.0350 (54); 191.0565 (53)	1
	Caffeoyl quinide	12.95	335.0765	C16H16O8	-1.38	161.0241 (100); 133.0290 (50); 135.0444 (18)	2
	Coumaroyl quinic acid	7.01	337.0918	C16H18O8	-1.99	163.0403 (100); 119.0502 (82); 191.0561 (16)	2
	Vanilloyl hexose	7.67	329.0904	C14H18O9	-2.1	167.0350 (100); 123.0470 (34)	2
	3,4-dihydroxybenzoic acid	3.48	153.0184	C7H6O4	-2.61	109.0280 (100)	1
Flavonols	Quercetin-pentoside-hexoside	16.26	595.1302	C26H28O16	-0.21	300.0275 (100); 271.0233 (14); 255.0286 (7)	2
	Quercetin hexoside deoxyhexoside 1	17.01	609.1432	C27H30O16	-1.89	300.0275 (100); 271.0233 (12); 255.0281 (6)	2
	Quercetin-3-galactoside	17.27	463.0883	C21H20O12	-2.53	300.0275 (100); 271.0247 (39); 255.0297 (16)	1
	Quercetin-3-rutinoside	17.51	609.1453	C27H30O16	-0.98	300.0275 (100); 271.0238 (11)	1
	Quercetin-3-glucoside	17.80	463.0893	C21H20O12	-2.24	300.0275 (100); 271.0249 (38); 255.0300 (16)	1
	Quercetin-dihexoside 1	13.88	625.1396	C27H30O17	-0.01	300.0275 (100); 271.0237 (13)	2
	Quercetin-dihexoside 2	14.26	625.1417	C27H30O17	0.14	300.0275 (100); 271.0243 (12)	2
	Quercetin	23.46	301.0356	C15H10O7	2.66	151.0050 (100)	1
	Quercetin-hexoside-deoxyhexoside 2	19.22	609.1449	C27H30O16	-1.91	315.0477 (100); 314.0428 (37); 299.0205 (37); 271.0213 (24); 285.0393 (13)	2
	Quercetin-pentoside	18.83	433.0763	C20H18O11	-1.85	300.0275 (100); 271.0239 (55); 255.0292 (23)	2
	Isorhametin-hexoside-deoxyhexoside 1	19.83	623.1608	C28H32O16	-1.55	315.0511 (100); 314.0417 (55)	2
	Isorhametin-hexoside-deoxyhexoside 2	20.10	623.1615	C28H32O16	-0.30	315.0486 (100); 314.0384 (33)	2

\* Identification levels were established according to Sumner et al. Level 1 identifications were validated by an authentic standard, while level 2 identifications were proposed according to exact mass, MS/MS fragmentation and UV absorption.

**Table S3.** Composition in flavan-3-ols and PACs after phloroglucinolysis. Values are expressed in g/100 g of extract (mean  $\pm$  standard deviation).

	Concentration (g /100 g)			
	Aronia Extract (AE)	A1 Fraction	A2 Fraction	A3 Fraction
Catechin	0.014 $\pm$ 0.001	0.033 $\pm$ 0.001	0.074 $\pm$ 0.001	ND
Epicatechin	0.125 $\pm$ 0.004	0.210 $\pm$ 0.003	0.431 $\pm$ 0.010	0.081 $\pm$ 0.002
Flavan-3-ols monomers total	0.139 $\pm$ 0.004	0.242 $\pm$ 0.004	0.505 $\pm$ 0.010	0.081 $\pm$ 0.002
Procyanidin B2	0.221 $\pm$ 0.001	0.380 $\pm$ 0.002	0.150 $\pm$ 0.004	0.011 $\pm$ 0.001
PACs total	21.95 $\pm$ 0.02	1.69 $\pm$ 0.10	15.15 $\pm$ 0.04	50.32 $\pm$ 0.05
Mean DP	29 $\pm$ 0.6	3 $\pm$ 0.6	11 $\pm$ 0.7	74 $\pm$ 6

**Table S4.** Anthocyanin composition of aronia extract and its polyphenolic fractions. Values are expressed in mg/g of extract (mean  $\pm$  standard deviation).

	Concentration (mg /g)			
	Aronia Extract (AE)	A1 Fraction	A2 Fraction	A3 Fraction
Cyanidin-3-galactoside	31.8 $\pm$ 0.9	64 $\pm$ 3.9	0.89 $\pm$ 0.03	0.33 $\pm$ 0.002
Cyanidin-3-glucoside	2.44 $\pm$ 0.05	5.0 $\pm$ 0.3	0.168 $\pm$ 0.011	0.022 $\pm$ 0.001
Cyanidin-3-arabinoside	13.2 $\pm$ 0.3	28.6 $\pm$ 1.8	0.423 $\pm$ 0.006	0.171 $\pm$ 0.003
Cyanidin-3-xyloside	2.21 $\pm$ 0.06	4.9 $\pm$ 0.3	0.081 $\pm$ 0.001	0.029 $\pm$ 0.001
Peonidin-3-galactoside	ND	ND	ND	ND
Peonidin-3-glucoside	ND	ND	ND	ND
Peonidin-3-arabinoside	ND	ND	ND	ND
Pelagornidin-3-glucoside	ND	ND	ND	ND
Pelagornidin-3-rutinoside	ND	ND	ND	ND
<b>Total Anthocyanins</b>	<b>49.7 <math>\pm</math> 1.3</b>	<b>102 <math>\pm</math> 6</b>	<b>1.56 <math>\pm</math> 0.05</b>	<b>0.552 <math>\pm</math> 0.007</b>