

1S. RP-HPLC quantification of phenolic compounds of flours

mg g d.m.-1	MeOH/H ₂ O 70/30 EXTRACTS			MeOH/HCl 97/3 EXTRACTS		
	WF	AF	GP	WF	AF	GP
Non-anthocyanidic phenols						
HYDROXYBENZOIC ACIDS	35 %	11 %	9 %		0.003 %	1 %
Gallic acid	0.109 ± 0.009	0.0427 ± 0.003	0.123 ± 0.004		0.002 ± 0.0003	0.029 ± 0.003
Syringic acid	0.014 ± 0.009	0.0086 ± 0.001	0.117 ± 0.005			0.156 ± 0.013
HYDROXYCINNAMIC ACIDS	31 %	7 %	23 %		0.01 %	29 %
Cinamic acid						
Caftaric acid						6.9 ± 0.23
Caffeic acid	0.0982 ± 0.0004		0.64 ± 0.01			0.031 ± 0.004
Ferulic acid	0.005 ± 0.002	0.027 ± 0.001			0.0088 ± 0.0002	0.0127 ± 0.0005
p-coumaric acid	0.004 ± 0.001	0.006 ± 0.0003				
STILBENES			0.5 %		0.05 %	0.1 %
Trans-piceatannol					0.0311 ± 0.0005	
pterostilbene					0.003 ± 0.002	
trans-resveratrol			0.0148 ± 0.0016			0.0196 ± 0.0004
FLAVANOLS	25 %	20 %	51 %	100 %	99 %	69 %
Procyanidin B1			0.045 ± 0.004			0.0043 ± 0.0002
(+)-catechin			0.76 ± 0.09			0.0232 ± 0.0005
Procyanidin B2			0.088 ± 0.008		0.0168 ± 0.0006	0.0021 ± 0.0001
(-)-epicatechin			0.32 ± 0.05			0.0024 ± 0.0001
(-)-epigallocatechin				14 ± 2	63 ± 4	16.4 ± 0.5
(-)-epigallocatechin gallate		0.098 ± 0.001		0.0047 ± 0.0001	0.0197 ± 0.0009	
(-)-gallocatechin gallate	0.0892 ± 0.0004		0.094 ± 0.008	0.0244 ± 0.0002	0.0769 ± 0.0027	
Astilbin			0.104 ± 0.001			
FLAVANONES		27 %	2 %		0.2 %	
Naringin		0.0305 ± 0.0012	0.063 ± 0.0008		0.108 ± 0.009	
Naringenin		0.09768 ± 0.0036				
FLAVONOLS	9 %	12 %	15 %		0.3 %	0.6 %
Rutin-trihidrate	0.032 ± 0.006	0.031 ± 0.002				
Quercetin-3-glucoside		0.009 ± 0.002	0.065 ± 0.005		0.16 ± 0.03	
Kaempferol-3-glucoside		0.01622 ± 0.00002	0.164 ± 0.004			0.032 ± 0.003
Myricetin			0.052 ± 0.001			0.072 ± 0.007
Quercetin hydrate			0.133 ± 0.01			0.031 ± 0.002
Quercetin 3-β-D-galactoside						
CHALCONES		24 %				
Phloridzin		0.113 ± 0.006				
OTHER COMPOUNDS					0.04 %	0.2 %
OH-Tyrosol					0.027 ± 0.003	0.044 ± 0.003
Tyrosol						0.0023 ± 0.0002
TOTAL (Non-anthocyanidic)	0.4	0.5	3	14	63	24

EXTRACTS	MeOH/H ₂ O 70/30		MeOH/HCl 97/3	
	GP	GP	GP	GP
Anthocyanidic polyphenols				
Glucosylated	57 %	92 %		
Del-3-G	0.37 ± 0.01	0.28 ± 0.02		
Cya-3-G	0.131 ± 0.003	0.15 ± 0.01		
Pet-3-G	0.436 ± 0.003	0.9 ± 0.1		
Peo-3-G	0.4 ± 0.02	0.9 ± 0.1		
Mal-3-G	3.25 ± 0.08	9.0 ± 0.7		
Acylylated	29 %	3 %		
Del-3-acet	0.175 ± 0.005			
Peo-3-acet	0.234 ± 0.002	0.023 ± 0.004		
Pet-3-acet		0.321 ± 0.003		
Mal-3-acet	1.9 ± 0.08	0.021 ± 0.002		
Coumaroylated	14 %	5 %		
Pet-3-p.cou	0.108 ± 0.001			
Cya-3-p.cou	0.322 ± 0.011	0.17 ± 0.04		
Peo-3-p.cou	0.131 ± 0.004	0.05 ± 0.01		
Mal-3-p.cou	0.536 ± 0.015	0.4 ± 0.1		
TOTAL (Anthocyanidic)	8	12		

2S. RP-HPLC quantification of phenolic compounds of breads

mg g d.m.-1	MeOH/H ₂ O 70/30 EXTRACTS				MeOH/HCl 97/3 EXTRACTS			
	C	A20	GP5	A20GP5	C	A20	GP5	A20GP5
Non-anthocyanidic phenols	8 %	14 %	26 %	34 %				
HYDROXYBENZOIC ACIDS							0.03 %	0.03 %
Gallic acid	0.07 ± 0.02	0.3 ± 0.2	0.2 ± 0.1	0.27 ± 0.17				0.007 ± 0.002
Syringic acid	0.14 ± 0.14	0.2 ± 0.1	0.065 ± 0.001	0.057 ± 0.002			0.0134 ± 0.0005	0.0149 ± 0.0008
HYDROXYCINNAMIC ACIDS	76 %	74 %	29 %	30 %		0.04 %	0.3 %	0.2 %
Cinamic acid								
Caffaric acid						0.013 ± 0.002	0.129 ± 0.002	0.114 ± 0.003
Caffeic acid	2.2 ± 0.1	2.5 ± 0.3	0.3 ± 0.1	0.3 ± 0.1		0.014 ± 0.004		0.005 ± 0.002
Ferulic acid		0.007 ± 0.001	0.0078 ± 0.002	0.0029 ± 0.0004				
p-coumaric acid		0.0091 ± 0.001	0.0037 ± 0.0006	0.011 ± 0.001				
STILBENES						0.01 %		0.01 %
Trans-piceatannol						0.0056 ± 0.0002		0.00685 ± 0.00003
pterostilbene								
trans-resveratrol								
FLAVANOLS	13 %	4 %	42 %	34 %	99.9 %	99.9 %	99.7 %	99.7 %
Procyanidin B1	0.13 ± 0.05	0.089 ± 0.005	0.08 ± 0.01	0.069 ± 0.005				
(+)-catechin			0.16 ± 0.02	0.11 ± 0.03				
Procyanidin B2			0.0230 ± 0.0001	0.016 ± 0.004		0.0031 ± 0.0003	0.0022 ± 0.0001	0.0044 ± 0.0002
(-)-epicatechin			0.07 ± 0.01	0.05 ± 0.01			0.0017 ± 0.0001	
(-)-epigallocatechin					33 ± 2	62 ± 21	51 ± 3	74 ± 6
(-)-epigallocatechin gallate		0.057 ± 0.006				0.01 ± 0.003		
(-)-gallocatechin gallate	0.09 ± 0.01		0.083 ± 0.013	0.065 ± 0.004		0.117 ± 0.0007		
Astilbin	0.15 ± 0.04		0.028 ± 0.003	0.018 ± 0.001				
FLAVANONES		2 %	2 %	2 %		0.03 %		0.02 %
Naringin		0.021 ± 0.007	0.0177 ± 0.0004	0.018 ± 0.001		0.018 ± 0.003		0.017 ± 0.003
Naringenin		0.038 ± 0.008						
FLAVONOLS	4 %	5 %	1 %		0.1 %	0.1 %		0.08 %
Rutin-trihidrate	0.046 ± 0.008	0.066 ± 0.002	0.0065 ± 0.0005					
Quercetin-3-glucoside					0.018 ± 0.003	0.032 ± 0.005		0.033 ± 0.001
Kaempferol-3-glucoside			0.0073 ± 0.0003					
Myricetin	0.072 ± 0.006	0.1 ± 0.05						0.0132 ± 0.0002
Quercetin hydrate								0.0145 ± 0.0001
Quercetin 3-β-D-galactoside								
CHALCONES		1 %						
Phloridzin		0.03 ± 0.01						
OTHER COMPOUNDS								0.002 %
OH-Tyrosol								0.00085 ± 0.00002
Tyrosol								0.00095 ± 0.00008
TOTAL (Non-anthocyanidic)	2.9	3.4	1	1	33	62	51	74

EXTRACTS	MeOH/H ₂ O 70/30		MeOH/HCl 97/3	
	GP5	A20GP5	GP5	A20GP5
Anthocyanidic polyphenols	49 %	49 %	69 %	37 %
Glucosylated				
Del-3-G	0.126 ± 0.001	0.122 ± 0.001	0.13 ± 0.01	
Cya-3-G	0.1186 ± 0.0001	0.116 ± 0.001	0.0354 ± 0.002	
Pet-3-G	0.132 ± 0.003	0.1278 ± 0.0004	0.5 ± 0.05	
Peo-3-G	0.132 ± 0.003	0.1300 ± 0.0001	0.14 ± 0.01	
Mal-3-G	0.29 ± 0.02	0.27 ± 0.02	2.0 ± 0.2	0.0203 ± 0.0005
Acylated	28 %	27 %	5 %	63 %
Del-3-acet	0.1175 ± 0.0003	0.117 ± 0.001	0.10 ± 0.01	
Peo-3-acet	0.122 ± 0.002	0.119 ± 0.002	0.07 ± 0.01	0.0195 ± 0.0005
Pet-3-acet			0.07 ± 0.01	
Mal-3-acet	0.21 ± 0.01	0.186 ± 0.007	0.021 ± 0.001	0.0153 ± 0.0003
Coumaroylated	23 %	24 %	26 %	
Pet-3-p cou				
Cya-3-p cou	0.1233 ± 0.0005	0.123 ± 0.002	0.08 ± 0.01	
Peo-3-p cou	0.1169 ± 0.0005	0.117 ± 0.001	0.09 ± 0.01	
Mal-3-p cou	0.136 ± 0.004	0.133 ± 0.001	0.9 ± 0.1	
TOTAL (Anthocyanidic)	1.6	1.6	4	0.06

3S. RP-HPLC quantification of phenolic compounds of gastrointestinal digests of breads

mg g d.m.-1	MeOH/H ₂ O 70/30 EXTRACTS				MeOH/HCl 97/3 EXTRACTS			
	DC	DA20	DGP5	DA20GP5	DC	DA20	DGP5	DA20GP5
Non-anthocyanidic phenols								
HYDROXYBENZOIC ACIDS		18 %	25 %			0.1 %	0.01 %	0.005 %
Gallic acid		0.022 ± 0.001	0.030 ± 0.001			0.42 ± 0.02	0.07 ± 0.02	0.0015 ± 0.0005
Syringic acid			0.15 ± 0.07				0.0007 ± 0.0003	0.013 ± 0.006
HYDROXYCINNAMIC ACIDS	8 %		53 %			0.02 %		0.03 %
Cinamic acid								
Caftaric acid						0.0393 ± 0.0001	0.133 ± 0.003	0.07 ± 0.01
Caffeic acid			0.3 ± 0.2			0.032 ± 0.002		0.02 ± 0.01
Ferulic acid	0.016 ± 0.001		0.0124 ± 0.0004					
p-coumaric acid	0.0039 ± 0.003		0.0156 ± 0.0002					
STILBENES						0.03 %	0.1 %	0.04 %
Trans-piceatannol						0.0071 ± 0.0006		
pterostilbeno						0.088 ± 0.002	0.473 ± 0.008	0.10 ± 0.02
trans-resveratrol								
FLAVANOLS	18 %	62 %	22 %	85 %	99.98 %	99.8 %	99.88 %	99.9 %
Procyanidin B1			0.040 ± 0.001					
(+)-catechin			0.024 ± 0.002					
Procyanidin B2		0.0165 ± 0.0003	0.027 ± 0.004		0.0031 ± 0.0004	0.01 ± 0.001		0.0021 ± 0.0002
(-)-epicatechin			0.025 ± 0.003		0.07 ± 0.03	0.054 ± 0.002	0.0056 ± 0.0001	0.004 ± 0.002
(-)-epigallocatechin					480 ± 151	354 ± 8	576 ± 2	268 ± 6
(-)-epigallocatechin gallate	0.043 ± 0.002			0.078 ± 0.001	0.03 ± 0.02		0.043 ± 0.001	0.025 ± 0.001
(-)-gallocatechin gallate		0.060 ± 0.001		0.062 ± 0.001				
Astilbin								
FLAVANONES						0.004 %	0.003 %	0.003 %
Naringin							0.0179 ± 0.0002	0.007 ± 0.003
Naringenin						0.015 ± 0.002		
FLAVONOLS	73 %	20 %	0.1 %	15 %	0.002 %		0.001 %	0.005 %
Rutin-trihidrate	0.174 ± 0.01			0.024 ± 0.006				0.015 ± 0.008
Quercetin-3-glucoside		0.025 ± 0.006	0.0010 ± 0.0003					
Kaempferol-3-glucoside								
Myricetin					0.0077 ± 0.0001		0.00679 ± 0.00002	
Quercetin hydrate								
Quercetin 3-β-D-galactoside								
CHALCONES								
Phloridzin								
OTHER COMPOUNDS						0.02 %		0.002 %
OH-Tyrosol						0.061 ± 0.006		0.005 ± 0.001
Tyrosol								
TOTAL (Non-anthocyanidic)	0.2	0.1	0.7	0.16	480	355	577	268

EXTRACTS	MeOH/H ₂ O 70/30		MeOH/HCl 97/3	
	DGP5	DA20GP5	DGP5	DA20GP5
Anthocyanidic polyphenols	35 %	62 %	63 %	64 %
Glucosylated				
Del-3-G		0.154 ± 0.004		0.0163 ± 0.0005
Cya-3-G				
Pet-3-G		0.154 ± 0.004	0.0109 ± 0.0003	
Peo-3-G		0.1501 ± 0.0003	0.012 ± 0.0003	0.012 ± 0.002
Mal-3-G	0.104 ± 0.001	0.288 ± 0.009	0.037 ± 0.002	0.016 ± 0.001
Acyalted	32 %	25 %	12 %	
Del-3-acet				
Peo-3-acet				
Pet-3-acet		0.151 ± 0.02	0.01168 ± 0.00003	
Mal-3-acet	0.095 ± 0.002	0.153 ± 0.03		
Coumaroylated	32 %	13 %	24 %	36 %
Pet-3-p cou				
Cya-3-p cou				
Peo-3-p cou			0.0108 ± 0.0003	0.0129 ± 0.0003
Mal-3-p cou	0.095 ± 0.004	0.161 ± 0.004	0.0122 ± 0.0003	0.012 ± 0.002
TOTAL (Anthocyanidic)	0.3	1	0.1	0.07

4S. RP-HPLC standard phenolic compounds

Non-anthocyanidic polyphenols	Source
HYDROXYBENZOIC ACIDS	
Gallic acid	Sigma-Aldrich
Syringic acid	Sigma-Aldrich
HYDROXYCINNAMIC ACIDS	
Cinamic acid	Sigma-Aldrich
Caftaric acid	Sigma-Aldrich
Caffeic acid	Sigma-Aldrich
Ferulic acid	Sigma-Aldrich
p-coumaric acid	Sigma-Aldrich
STILBENES	
Trans-piceatannol	Sigma-Aldrich
pterostilbeno	Sigma-Aldrich
trans-resveratrol	Sigma-Aldrich
FLAVANOLS	
Procyanidin B1	Sigma-Aldrich
(+)-catechin	Sigma-Aldrich
Procyanidin B2	Sigma-Aldrich
(-)-epicatechin	Sigma-Aldrich
(-)-epigallocatechin	Sigma-Aldrich
(-)-epigallocatechin gallate	Sigma-Aldrich
(-)-gallocatechin gallate	Sigma-Aldrich
Astilbin	Sigma-Aldrich
FLAVANONES	
Naringin	Sigma-Aldrich
Naringenin	Sigma-Aldrich
FLAVONOLS	
Rutin-trihidrate	Sigma-Aldrich
Quercetin-3-glucoside	Sigma-Aldrich
Kaempferol-3-glucoside	Sigma-Aldrich
Myricetin	Sigma-Aldrich
Quercetin hydrate	Sigma-Aldrich
quercetin 3-β-D-galactoside	Sigma-Aldrich
CHALCONES	
Phloridzin	Sigma-Aldrich
OTHER COMPOUNDS	
OH-Tyrosol	Fluka (Buchs, Switzerland)
Tyrosol	Fluka (Buchs, Switzerland)

Anthocyanidic polyphenols

Malvidin-3-O-glucoside chloride	Sigma-Aldrich	Mal-3-G
Delphinidin-3-glycoside	*	Del-3-G
Cyanidin-3-glycoside	*	Cya-3-G
Petunidin-3-glycoside	*	Pet-3-G
Peonidin-3-glycoside	*	Peo-3-G
Delphinidin-3-acetylglucoside	*	Del-3-acet
Petunidin-3-acetylglucoside	*	Pet-3-acet
Peonidin-3-acetylglucoside	*	Peo-3-acet
Malvinidin-3-acetylglucoside	*	Mal-3-acet
Cyanidin-3-p-coumaroyl glycoside	*	Cya-3-p cou
Petunidin-3-p-coumaroyl glycoside	*	Pet-3-p cou
Peonidin-3-p-coumaroyl glycoside	*	Peo-3-p cou
Malvinidin-3-p-coumaroyl glycoside	*	Mal-3-p cou

*the content of individual anthocyanins was expressed as malvidin-3-glucoside equivalents using an external standard calibration curve for this compound ($1-250\text{mg L}^{-1}$, $r^2 = 0.997$).

4S. Acronyms

Abbreviation	
A20	Bread with 20% amaranth flour replacement
A20GP5	Bread with 20% amaranth flour + 5% red grape peel flour replacement
AAPH	2,2'-Azobis(2-methylpropionamidine) dihydrochloride
ABTS	2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)
AF	Amaranth flour
a_w	water activity
C	100% wheat flour bread (CONTROL)
DA20	Bread with 20% amaranth flour replacement digest
DA20GP5	Bread with 20% amaranth flour + 5% red grape peel flour replacement digest
DC	100% wheat flour bread digest
DF	Dietary fibre
DGP5	Bread with 5% red grape peel flour replacement digest
d.m.	dry basis
EC	(-)-epicatechin
EGC	(-)-epigallocatechin
EGCG	(-)-epigallocatechin gallate
ESP	Esterified phenol fraction
FA	Formic acid
FP	Free phenol fraction
GAE	Gallic acid equivalents
GCG	(-)-gallocatechin gallate
GP	Red grape peel flour
GP5	Bread with 5% red grape peel flour replacement
IDF	Insoluble dietary fibre
LIP	Linked insoluble phenol fraction
mDP	mean degree of polymerisation
MeCN	Acetonitrile
MeOH	Methanol
ORAC	Oxygen Radical Absorption Capacity
PC	Phenolic compounds
SDF	Soluble dietary fibre
SGID	Simulated gastrointestinal digestion
TDF	Total dietary fibre
TE	Trolox equivalents
TP	Total phenols
WF	Wheat flour