

TITLE: “ Industrial and culinary treatments applied to Piquillo pepper (*Capsicum annuum* cv. *Piquillo*) impact positively on (poly)phenols bioaccessibility and gut microbiota catabolism”

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SUPPLEMENTARY MATERIALS

Table S1. Concentration of electrolyte stock solutions and simulated salivary fluid (SSF) simulated gastric fluid (SGF) and simulated intestinal fluid (SIF) for *in vitro* gastrointestinal digestion.

Compound	MW	Stock solution		SSF	SGF	SIF
		mol/L	g/50 ml	(500 mL)	(500 mL)	(500 mL)
				mL of stock solution		
KCl	74.55	0.50	1.85	18.87	8.62	8.50
KH₂PO₄	136.09	0.50	3.40	4.62	1.12	1.00
NaHCO₃	84.01	1.00	4.20	8.50	15.62	53.12
NaCl	58.40	2.00	5.85	-	14.75	12.00
MgCl₂ (H₂O)₆	203.21	0.15	1.52	0.62	0.50	1.37
(NH₄)₂CO₃	96.09	0.50	2.40	0.07	0.62	-
HCl	36.46	6.00	-	0.11	1.62	0.87
CaCl₂	147.02	0.30	2.20	0.03	6.25 x10 ⁻³	0.05

* MW= Molecular weight

Table S2. Mass spectrometric identification parameters of (poly)phenol compounds identified in Piquillo pepper of Lodosa after *in vitro* gastrointestinal digestion and colonic fermentation determined by HPLC-ESI-MS/MS and their standardized nomenclature proposed by Kay et al., (33).

Recommended name	Other common names	Abbreviation	Rt	[M-H] ⁻ (m/z)	MS ² quantifier	MS ² qualifier	CE (eV)
Benzenediols and triols							
Benzene -1,2-diol	1,2-Dihydroxybenzene, Catechol	Benz-1,2-diol	3.15	109	108	91	-25
Benzene -1,2,3-triol	1,2,3-Trihydroxybenzene, Pyrogallol	Benz-1,2,3-triol	1.30	125	79	81	-25
Benzoic acids							
3-Hydroxybenzoic acid	-	3-OH-BA	6.24	137	93	109	-20
4-Hydroxybenzoic acid	-	4-OH-BA	4.12	137	93		-15
2,5-Dihydroxybenzoic acid	-	2,5-diOH-BA	4.40	153	108	109	-30
3,4-Dihydroxybenzoic acid	Protocatechuic acid	3,4-diOH-BA	2.20	153	109	91	-35
3-Methoxybenzoic acid 4-O-glucoside	Vanillic acid glucoside	3-MetOH-BA-4-O-GlucSD	3.10	329	167	209	-25
Cinnamic acids							
4'-Hydroxycinnamic acid	p-coumaric acid	4'-OH-CA	8.70	163	119	93	-30
Cinnamic-4'-O-glucoside	Coumaric acid glucoside	CA-4'-O-GlucSD	5.80	325	163	119	-25
3',4'-Dihydroxycinnamic acid	Caffeic acid	3',4'-diOH-CA	6.31	179	135	134	-30
4'-Hydroxycinnamic-3-O-glucoside	Caffeic acid glucoside	4'-OH-CA-3'-O-GlucSD	6.20	341	179	135	-20
4'-Hydroxy-3'-methoxycinnamic acid	Ferulic acid	4'-OH-3'-MetOH-CA	9.45	193	134	178	-20
3'-Hydroxy-4'-methoxycinnamic acid	Isoferulic acid	3'-OH-4'-MetOH-CA	9.50	193	178	134	-15
3'-Methoxycinnamic-4'-O-glucoside	Ferulic acid glucoside	3'-MetOH-CA-4'-O-GlucSD	7.10	355	175	193	-20
4'-Hydroxy-3',5'-dimethoxycinnamic acid	Sinapic acid	4'-OH-3',5'-diMetOH-CA	9.60	223	193	121	-30
3',5'-Dimethoxycinnamic-4'-O-glucoside	Sinapic acid glucoside	3',5'-diMetOH-CA-4'-O-GlucSD	7.50	385	223	164	-25
Phenylpropanoic acids							
3-Phenylpropanoic acid	3-Phenylpropionic acid	3-PrA	14.55	149	105		-15
3-(3'-Hydroxyphenyl)propanoic acid		3-(3'-OH-ph)PrA	9.20	165	121	119	-15
3-(3',4'-Dihydroxyphenyl)propanoic acid	Dihydrocaffeic acid	3-(3',4'-diOH-ph)-PrA	5.60	181	59	137	-25
3-(4'-Hydroxy-3'-methoxyphenyl)propanoic acid	Dihydroferulic acid	3-(4'-OH-3'-MetOH-ph)PrA	9.00	195	136	121	-30
Phenylacetic acids							
Phenylacetic acid	Phenylacetic acid	PhA	10.20	135	91	83	-15
3'-Hydroxyphenylacetic acid	-	3'-OH-PhA	6.70	151	107	93	-10
4'-Hydroxyphenylacetic acid	-	4'-OH-PhA	5.42	151	107	65	-15
4'-Hydroxy-3'-methoxyphenylacetic acid	Homovanillic acid	4'-OH-3'-MetOH-phAc	7.30	181	137	163	-25
Others							
2-(3'-Hydroxyphenyl)ethanol	Hydroxytyrosol	2'-OH-4'MetOH-Ac-phON	2.10	153	123	108	-30
4-Hydroxy-1,2-benzopyrone	4-Hydroxycoumarin	4-OH-1,2-BenzPyON	6.50	161	117	133	-30
2'-Hydroxy-4'-methoxyacetophenone	Paeonol	2'-OH-4'MetOH-Ac-phON	8.70	165	150		-25
Acyl-quinic acids							
5-Caffeoylquinic acid	Chlorogenic acid	5-CQA	5.85	353	191	179	-20
4-Caffeoylquinic acid	Cryptochlorogenic acid	4-CQA	6.73	353	173	179	-30

Table 2 (Continued)

Recommended name	Other common names	Abbreviation	Rt	[M-H] ⁻ (m/z)	MS ² quantifier	MS ² qualifier	CE (eV)
FLAVONOIDS							
Flavonols							
Quercetin	Quercetin	Quercetin	15.92	301	151	179	-30
Quercetin-3- <i>O</i> -rutinoside	Rutin	Querc-3- <i>O</i> -Rut	9.96	609	301	179	-50
Quercetin-3- <i>O</i> -glucoside	Isoquercitrin	Querc-3- <i>O</i> -GlucSD	10.25	463	300	301	-35
Quercetin-3- <i>O</i> -rhamnoside	Quercitrin	Querc-3- <i>O</i> -Rha	12.28	447	301	283	-40
Quercetin-acetyl-glucoside	-	Querc-Ace-GlucSD	11.50	505	300	271	-30
Quercetin-3- <i>O</i> -glucoside-7- <i>O</i> -rhamnoside	-	Querc-3- <i>O</i> -GlucSD-7- <i>O</i> -Rha	8.30	609	301	463	-40
Quercetin-3- <i>O</i> -sambubioside-7- <i>O</i> -rhamnoside	-	Querc-3- <i>O</i> -Samb-7- <i>O</i> -Rha	8.4	741	299	301	-65
Isorhamnetin	-	Isorhamnetin	18.30	315	300	151	-30
Isorhamnetin-3- <i>O</i> -glucoside	-	IsorhTN-3- <i>O</i> -GlucSD	12.49	477	314	271	-25
Kaempferol	-	Kaempferol	18.18	285	93	65	-50
Kaempferol-7- <i>O</i> -glucoside	-	Kmpf-7- <i>O</i> -GlucSD	12.72	447	285	284	-30
Kaempferol-malonyl-glucoside	-	Kmpf-MaO-GlucSD	13.22	533	489	285	-30
Flavones							
Luteolin	-	Luteolin	15.83	285	133	151	-50
Luteolin-7- <i>O</i> -glucoside	-	Lut-7- <i>O</i> -GlucSD	10.32	447	285	327	-30
Luteolin-8- <i>C</i> -glucoside	Orientin	Lut-8- <i>C</i> -GlucSD	9.38	447	327	297	-35
Luteolin-6- <i>C</i> -glucoside	Isoorientin	Lut-6- <i>C</i> -GlucSD	9.18	447	327	257	-25
Luteolin-6- <i>C</i> -hexoside-8- <i>C</i> -pentoside	-	Lut-6- <i>C</i> -Hex-8- <i>C</i> -Pent	8.50	579	459	489	-30
Luteolin-6- <i>C</i> -pentoside-8- <i>C</i> -hexoside	-	Lut-6- <i>C</i> -Pent-8- <i>C</i> -Hex	8.90	579	489	459	-30
Luteolin-6,8- <i>C</i> -diglucoside	Lucenin-2	Lut-6,8- <i>C</i> -diGlucSD	8.10	609	369	399	-55
Luteolin-7- <i>O</i> -(2- <i>O</i> -apiosyl)glucoside	-	Lut-7- <i>O</i> -(2- <i>O</i> -Ap)GlucSD	10.26	579	285	447	-40
Luteolin-7- <i>O</i> -(2- <i>O</i> -apiosylacetyl)glucoside	-	Lut-7- <i>O</i> -(2- <i>O</i> -Ap-Ace)GlucSD	13.01	621	285	489	-55
Luteolin-7- <i>O</i> -(2- <i>O</i> -apiosyl-6- <i>O</i> -malonyl)glucoside	-	Lut-7- <i>O</i> -(2- <i>O</i> -Ap-6- <i>O</i> -MaO)GlucSD	13.20	665	621	285	-40
Chrysoeriol 6- <i>C</i> -glucoside	Isoscoparin	ChryOL 6- <i>C</i> -GlucSD	10.44	461	341	371	-30
Apigenin-8- <i>C</i> -glucoside	Vitexin	Apig-8- <i>C</i> -GlucSD	9.94	431	311	283	-30
Apigenin-6,8- <i>C</i> -diglucoside	Vicenin-2	Apig-6,8- <i>C</i> -diGlucSD	8.56	593	353	383	-45
Apigenin-pentoside-hexoside	-	Apig-Pent-Hex	8.98	563	383	473	-40
Apigenin-7- <i>O</i> -(2- <i>O</i> -apiosyl)glucoside	Apiin	Apig-7- <i>O</i> -(2- <i>O</i> -Ap)GlucSD	16.20	563	131	151	-40
Flavanones							
Naringenin	-	Naringenin	17.90	271	151	177	-40
Naringenin-7- <i>O</i> -Glucoside	-	NarGE-7- <i>O</i> -GlucSD	12.51	433	271	313	-20

Rt, retention time; m/z, mass-to-charge ratio; [M-H]⁻, Negatively charged molecular ion; MS², MS/MS transitions (qualifier and quantifier); CE, Collision energy.

Table S3. Content of individual (poly)phenolic compounds and derivatives from *in vitro* gastrointestinal digestion of raw and thermally treated Piquillo pepper. Results are expressed as μmol of (poly)phenol per g of pepper (dry matter) (mean \pm standard deviation, $n=3$)

Compound ^a	Raw	Grilled	Canned	Microwaved	Fried
NON FLAVONOIDS					
Benzenediols and triols					
Benz -1,2-diol	nd	0.177 \pm 0.007	0.131 \pm 0.003	0.139 \pm 0.001	0.109 \pm 0.003
Benz -1,2,3-triol	nd	0.014 \pm 0.001	0.013 \pm 0.000	0.011 \pm 0.001	0.010 \pm 0.001
Benzoic acid					
3-OH-BA	0.004 \pm 0.000	0.028 \pm 0.001	0.016 \pm 0.001	0.016 \pm 0.001	0.010 \pm 0.000
4-OH-BA	0.023 \pm 0.002	0.030 \pm 0.001	0.038 \pm 0.001	0.039 \pm 0.001	0.024 \pm 0.001
2,5-diOH-BA	0.005 \pm 0.000	0.006 \pm 0.000	0.006 \pm 0.000	0.005 \pm 0.000	0.003 \pm 0.000
3,4-diOH-BA	0.003 \pm 0.000	0.016 \pm 0.001	0.027 \pm 0.002	0.028 \pm 0.000	0.023 \pm 0.001
3-MetOH-BA-4-O-GlucSD	0.305 \pm 0.008	0.424 \pm 0.012	0.233 \pm 0.005	0.244 \pm 0.012	0.206 \pm 0.012
Cinnamic acids					
4'-OH-CA	0.015 \pm 0.000	0.010 \pm 0.000	0.006 \pm 0.000	0.007 \pm 0.000	0.006 \pm 0.000
CA-4'-O-GlucSD ^b	1.025 \pm 0.046	0.395 \pm 0.003	0.262 \pm 0.012	0.282 \pm 0.003	0.257 \pm 0.024
3',4'-diOH-CA	0.020 \pm 0.000	0.012 \pm 0.001	0.009 \pm 0.001	0.009 \pm 0.000	0.009 \pm 0.000
4'-OH-CA-3'-O-GlucSD	0.053 \pm 0.003	0.023 \pm 0.002	0.020 \pm 0.001	0.022 \pm 0.000	0.016 \pm 0.001
4'-OH-3'-MetOH-CA	0.126 \pm 0.003	0.055 \pm 0.001	0.041 \pm 0.001	0.045 \pm 0.000	0.044 \pm 0.001
3'-OH-4'-MetOH-CA	0.017 \pm 0.000	0.005 \pm 0.000	0.006 \pm 0.000	0.007 \pm 0.001	0.006 \pm 0.001
3'-MetOH-CA-4'-O-GlucSD ^b	0.074 \pm 0.002	0.116 \pm 0.001	0.076 \pm 0.007	0.068 \pm 0.004	0.036 \pm 0.003
4'-OH-3',5'-diMetOH-CA	0.031 \pm 0.002	0.009 \pm 0.000	0.011 \pm 0.000	0.011 \pm 0.000	0.009 \pm 0.000
3',5'-diMetOH-CA-4'-O-GlucSD ^b	0.026 \pm 0.002	0.016 \pm 0.000	0.012 \pm 0.000	0.013 \pm 0.000	0.012 \pm 0.000
Phenylpropanoic acids					
3-PrA ^c	0.693 \pm 0.014	0.729 \pm 0.010	0.820 \pm 0.024	0.871 \pm 0.010	0.649 \pm 0.009
3-(3-OH-ph)PrA ^c	0.007 \pm 0.000	0.007 \pm 0.001	0.007 \pm 0.000	0.009 \pm 0.001	0.006 \pm 0.000
3-(3',4'-diOH-ph)PrA	0.017 \pm 0.001	0.017 \pm 0.001	0.017 \pm 0.001	0.017 \pm 0.000	0.013 \pm 0.000
3-(4'-OH-3'-MetOH-ph)PrA ^c	0.101 \pm 0.003	0.082 \pm 0.004	0.098 \pm 0.001	0.098 \pm 0.004	0.069 \pm 0.002
Phenylacetic acids					
PhA ^c	1.078 \pm 0.049	1.053 \pm 0.065	1.187 \pm 0.029	1.298 \pm 0.025	0.757 \pm 0.007
4'-OH-3'-MetOH-PhA ^b	nd	1.419 \pm 0.021	1.010 \pm 0.027	1.192 \pm 0.085	1.103 \pm 0.016
Others					
2-(3'-OH-Ph)etOH ^c	Tr	Tr	Tr	Tr	0.006 \pm 0.000
4-OH-1,2-BenzPyON ^b	nd	Tr	Tr	Tr	Tr
2'-OH-4'methO-A-phON ^b	0.006 \pm 0.000	Tr	Tr	Tr	Tr
Acyl-quinic acids					
5-CQA	0.006 \pm 0.001	Tr	Tr	Tr	Tr
4-CQA	Tr	Tr	Tr	Tr	Tr
FLAVONOIDS					
Flavonols					
Querc	0.010 \pm 0.000	0.013 \pm 0.001	0.011 \pm 0.000	0.011 \pm 0.000	0.009 \pm 0.000
Querc 3-O-Rut	0.017 \pm 0.001	Tr	Tr	Tr	Tr
Querc 3-O-GlucSD	0.114 \pm 0.002	0.005 \pm 0.000	0.004 \pm 0.000	0.003 \pm 0.000	0.003 \pm 0.000
Querc 3-O-Rha	0.978 \pm 0.003	0.067 \pm 0.006	0.043 \pm 0.000	0.044 \pm 0.001	0.036 \pm 0.001
Querc-Ace-GlucSD ^b	0.018 \pm 0.002	Tr	Tr	Tr	Tr
Querc 3-O-GlucSD-7-O-Rha ^b	0.087 \pm 0.003	0.018 \pm 0.000	0.012 \pm 0.001	0.013 \pm 0.000	0.009 \pm 0.000
Querc 3-O-Samb-7-O-Rha ^b	0.010 \pm 0.001	Tr	Tr	Tr	Tr
IsorhTN	Tr	Tr	Tr	Tr	Tr
IsorhTN-3-O-GlucSD	0.016 \pm 0.001	Tr	Tr	Tr	Tr
Kmpf-MaO-GlucSD ^b	0.017 \pm 0.002	Tr	Tr	Tr	Tr

Table S3. (continued)

Compound ^a	Raw	Grilled	Canned	Microwaved	Fried
Flavones					
Lut	0.003 ± 0.000	0.005 ± 0.000	0.003 ± 0.000	0.003 ± 0.000	0.003 ± 0.000
Lut 7- <i>O</i> -GlucSD	0.006 ± 0.000	Tr	Tr	Tr	Tr
Lut 8- <i>C</i> -GlucSD	0.081 ± 0.002	0.017 ± 0.001	0.022 ± 0.001	0.023 ± 0.001	0.019 ± 0.001
Lut -6- <i>C</i> -GlucSD ^b	0.063 ± 0.002	0.010 ± 0.001	0.018 ± 0.000	0.018 ± 0.001	0.014 ± 0.001
Lut -6- <i>C</i> -Hex-8- <i>C</i> -Pent ^b	0.007 ± 0.001	0.005 ± 0.001	0.004 ± 0.000	0.004 ± 0.000	0.004 ± 0.000
Lut -6- <i>C</i> -Pent-8- <i>C</i> -Hex ^b	Tr	Tr	Tr	Tr	Tr
Lut -6,8- <i>C</i> -diGlucSD ^b	0.008 ± 0.001	0.005 ± 0.000	0.005 ± 0.000	0.006 ± 0.000	0.004 ± 0.000
Lut -7- <i>O</i> -(2- <i>O</i> -Ap)GlucSD ^b	0.062 ± 0.005	0.016 ± 0.001	0.034 ± 0.001	0.037 ± 0.002	0.032 ± 0.003
Lut 7- <i>O</i> -(2- <i>O</i> -Ap-Ac)GlucSD ^b	0.016 ± 0.001	Tr	Tr	Tr	Tr
Lut 7- <i>O</i> -(2- <i>O</i> -Ap-6- <i>O</i> -MaO)GlucSD ^b	0.852 ± 0.002	0.076 ± 0.006	0.042 ± 0.003	0.052 ± 0.001	0.036 ± 0.002
ChryOL 6- <i>C</i> -GlucSD ^b	Tr	Tr	Tr	Tr	Tr
Apig-8- <i>C</i> -GlucSD	Tr	Tr	Tr	Tr	Tr
Apig 6,8- <i>C</i> -diGlucSD	0.046 ± 0.001	0.025 ± 0.001	0.018 ± 0.000	0.020 ± 0.000	0.015 ± 0.000
Apig -Pent-Hex ^b	0.016 ± 0.001	0.008 ± 0.000	0.006 ± 0.000	0.007 ± 0.000	0.006 ± 0.000
Apig 7- <i>O</i> -(2- <i>O</i> -Ap)GlucSD ^b	0.059 ± 0.005	0.050 ± 0.003	0.070 ± 0.006	0.083 ± 0.001	0.072 ± 0.000
Flavanones					
NarGE ^b	0.068 ± 0.001	Tr	Tr	Tr	Tr
NarGE-7- <i>O</i> -GlucSD	0.030 ± 0.001	Tr	Tr	Tr	Tr

nd= not detected; Tr=traces. ^a Full compound names are shown in Table S2. ^b Tentatively identified and semiquantified compounds. ^c Compounds derived from simulated gastrointestinal digestion.

Table S4. Minor (poly)phenols and derivatives from 48h of colonic fermentation of raw and thermally treated Piquillo pepper (μmol of (poly)phenolic compound per g of pepper (dry matter) (mean \pm standard deviation, n=3).

Compound ^a	Raw	Grilled	Canned	Microwaved	Fried
NON-FLAVONOIDS					
Cinnamic acids					
4'-OH-CA					
T 0h ^d	0.015 \pm 0.000	0.010 \pm 0.000	0.006 \pm 0.000	0.007 \pm 0.000	0.006 \pm 0.000
T 2h	0.078 \pm 0.004	0.006 \pm 0.001	0.030 \pm 0.003	0.026 \pm 0.001	0.016 \pm 0.002
T 6h	Tr	Tr	Tr	Tr	Tr
T 24h	nd	nd	nd	nd	0.029 \pm 0.001
T 48h	nd	nd	nd	nd	Tr
4'-OH-CA-3'-O-GlucSD^b					
T 0h ^d	0.053 \pm 0.003	0.023 \pm 0.002	0.020 \pm 0.001	0.022 \pm 0.000	0.016 \pm 0.001
T 2h	0.041 \pm 0.003	0.006 \pm 0.000	0.021 \pm 0.001	0.010 \pm 0.000	0.025 \pm 0.000
T 6h	0.008 \pm 0.000	Tr	Tr	tr	Tr
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
3'-MetOH-CA- 4'-O-GlucSD^b					
T 0h ^d	0.074 \pm 0.002	0.116 \pm 0.001	0.076 \pm 0.007	0.068 \pm 0.004	0.036 \pm 0.003
T 2h	Tr	Tr	Tr	Tr	Tr
T 6h	nd	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	Nd
4'-OH-3',5'-diMetOH-CA					
T 0h ^d	0.031 \pm 0.002	0.009 \pm 0.000	0.011 \pm 0.000	0.011 \pm 0.000	0.009 \pm 0.000
T 2h	0.103 \pm 0.002	0.013 \pm 0.001	0.039 \pm 0.000	0.023 \pm 0.001	0.023 \pm 0.002
T 6h	0.015 \pm 0.000	0.011 \pm 0.000	0.019 \pm 0.002	0.023 \pm 0.003	0.012 \pm 0.001
T 24h	0.004 \pm 0.000	0.002 \pm 0.000	0.012 \pm 0.001	0.011 \pm 0.001	0.008 \pm 0.000
T 48h	0.010 \pm 0.001	0.005 \pm 0.000	0.009 \pm 0.001	0.014 \pm 0.001	0.008 \pm 0.000
3',5'-diMetOH-CA- 4'-O-GlucSD^b					
T 0h ^d	0.026 \pm 0.002	0.016 \pm 0.000	0.012 \pm 0.000	0.013 \pm 0.000	0.012 \pm 0.000
T 2h	0.008 \pm 0.000	Tr	nd	nd	Tr
T 6h	nd	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Other phenolics					
2-(3'-OH-Ph)etOH					
T 0h ^d	Tr	Tr	Tr	Tr	0.006 \pm 0.000
T 2h	0.005 \pm 0.001	Tr	Tr	0.002 \pm 0.000	Tr
T 6h	0.012 \pm 0.002	0.025 \pm 0.002	0.014 \pm 0.001	0.030 \pm 0.004	0.023 \pm 0.002
T 24h	0.047 \pm 0.003	0.059 \pm 0.002	0.020 \pm 0.003	0.048 \pm 0.004	0.016 \pm 0.004
T 48h	0.049 \pm 0.002	0.063 \pm 0.005	0.065 \pm 0.005	0.054 \pm 0.005	0.034 \pm 0.002
FLAVONOIDS					
Flavonols					
Querc 3-O-Rut					
T 0h ^d	0.017 \pm 0.001	Tr	Tr	Tr	Tr
T 2h	0.017 \pm 0.001	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Querc 3-O-GlucSD					
T 0h ^d	0.114 \pm 0.002	0.005 \pm 0.000	0.004 \pm 0.000	0.003 \pm 0.000	0.003 \pm 0.000
T 2h	0.142 \pm 0.009	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Querc 3- O-GlucSD-7-O-Rha^b					
T 0h ^d	0.087 \pm 0.003	0.018 \pm 0.000	0.012 \pm 0.001	0.013 \pm 0.000	0.009 \pm 0.000
T 2h	0.155 \pm 0.011	0.021 \pm 0.002	0.013 \pm 0.001	0.017 \pm 0.001	0.012 \pm 0.001
T 6h	nd	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Querc 3- O-Samb-7-O-Rha^b					
T 0h ^d	0.010 \pm 0.001	nd	nd	nd	nd
T 2h	0.021 \pm 0.001	nd	nd	nd	nd
T 6h	nd	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd

Table S4 (continued)

Compound^a	Raw	Grilled	Canned	Microwaved	Fried
Flavonols (continued)					
IsorhTN					
T 0h ^d	Tr	Tr	Tr	Tr	Tr
T 2h	nd	nd	nd	nd	nd
T 6h	nd	nd	0.004 ± 0.001	Tr	nd
T 24h	0.014 ± 0.001	0.018 ± 0.006	Tr	0.007 ± 0.000	nd
T 48h	0.003 ± 0.000	Tr	0.004 ± 0.000	Tr	nd
IsorhTN-3-O-glucoside					
T 0h ^d	0.016 ± 0.001	Tr	Tr	Tr	Tr
T 2h	0.066 ± 0.001	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Kmpf^c					
T 0h ^d	nd	nd	nd	nd	nd
T 2h	nd	Tr	nd	Tr	Tr
T 6h	0.013 ± 0.001	0.015 ± 0.001	0.014 ± 0.001	0.019 ± 0.002	0.006 ± 0.001
T 24h	0.017 ± 0.000	0.016 ± 0.001	0.009 ± 0.000	0.011 ± 0.000	0.003 ± 0.000
T 48h	0.017 ± 0.001	0.017 ± 0.001	0.018 ± 0.001	0.008 ± 0.001	0.004 ± 0.000
Kmpf-7-O-GlucSD^c					
T 0h ^d	nd	nd	nd	nd	nd
T 2h	0.005 ± 0.000	0.010 ± 0.001	0.007 ± 0.000	0.011 ± 0.000	0.007 ± 0.001
T 6h	0.008 ± 0.001	0.010 ± 0.001	0.012 ± 0.001	0.012 ± 0.001	0.009 ± 0.000
T 24h	0.008 ± 0.000	0.010 ± 0.001	0.010 ± 0.001	0.009 ± 0.001	0.006 ± 0.001
T 48h	0.007 ± 0.001	0.011 ± 0.001	0.012 ± 0.001	0.011 ± 0.001	0.010 ± 0.001
Flavones					
Lut 7-O-GlucSD					
T 0h ^d	0.006 ± 0.000	Tr	Tr	Tr	Tr
T 2h	0.177 ± 0.002	nd	nd	nd	nd
T 6h	0.020 ± 0.002	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Lut 8-C-GlucSD					
T 0h ^d	0.081 ± 0.002	0.017 ± 0.001	0.022 ± 0.001	0.023 ± 0.001	0.019 ± 0.001
T 2h	0.198 ± 0.005	0.005 ± 0.000	0.019 ± 0.001	0.014 ± 0.001	0.012 ± 0.001
T 6h	0.044 ± 0.006	0.005 ± 0.000	0.011 ± 0.001	0.010 ± 0.001	0.023 ± 0.000
T 24h	Tr	Tr	Tr	Tr	0.009 ± 0.001
T 48h	nd	nd	nd	nd	nd
Lut 6-C-GlucSD^b					
T 0h ^d	0.063 ± 0.002	0.010 ± 0.001	0.018 ± 0.000	0.018 ± 0.001	0.014 ± 0.001
T 2h	0.102 ± 0.005	0.009 ± 0.001	0.016 ± 0.001	0.016 ± 0.002	0.014 ± 0.001
T 6h	0.022 ± 0.001	0.007 ± 0.001	0.007 ± 0.000	0.010 ± 0.001	0.009 ± 0.001
T 24h	Tr	Tr	nd	Tr	Tr
T 48h	nd	nd	nd	nd	nd
Lut -6-C-Hex-8-C-Pent^b					
T 0h ^d	0.007 ± 0.001	0.005 ± 0.001	0.004 ± 0.000	0.004 ± 0.000	0.004 ± 0.000
T 2h	0.017 ± 0.001	Tr	Tr	Tr	Tr
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Lut -6-C-Pent-8-C-Hex^b					
T 0h ^d	Tr	Tr	Tr	Tr	Tr
T 2h	0.011 ± 0.001	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Lut -6,8-C-diGlucSD^b					
T 0h ^d	0.008 ± 0.001	0.005 ± 0.000	0.005 ± 0.000	0.006 ± 0.000	0.004 ± 0.000
T 2h	0.020 ± 0.001	0.004 ± 0.000	0.005 ± 0.000	0.005 ± 0.000	0.003 ± 0.000
T 6h	Tr	Tr	Tr	Tr	Tr
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
ChryOL 6-C-GlucSD^b					
T 0h ^d	Tr	Tr	Tr	Tr	Tr
T 2h	0.013 ± 0.001	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd

Table S4 (continued)

Compound ^a	Raw	Grilled	Canned	Microwaved	Fried
Flavones (continued)					
Apig-8-C-GlucSD					
T 0h ^d	Tr	Tr	Tr	Tr	Tr
T 2h	0.020 ± 0.002	nd	nd	nd	nd
T 6h	nd	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Apig-6,8-C-diGlucSD					
T 0h ^d	0.046 ± 0.001	0.025 ± 0.001	0.018 ± 0.000	0.020 ± 0.000	0.015 ± 0.000
T 2h	0.103 ± 0.003	0.008 ± 0.000	0.015 ± 0.000	0.013 ± 0.001	0.008 ± 0.001
T 6h	0.007 ± 0.001	Tr	Tr	Tr	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Apig -Pent-Hex^b					
T 0h ^d	0.016 ± 0.001	0.008 ± 0.000	0.006 ± 0.000	0.007 ± 0.000	0.006 ± 0.000
T 2h	0.047 ± 0.001	0.009 ± 0.001	0.008 ± 0.001	0.009 ± 0.001	0.009 ± 0.000
T 6h	0.008 ± 0.001	0.005 ± 0.000	0.005 ± 0.000	0.004 ± 0.000	0.005 ± 0.001
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd
Apig 7-O-(2-O-Ap)GlucSD^b					
T 0h ^d	0.059 ± 0.005	0.050 ± 0.003	0.070 ± 0.006	0.083 ± 0.001	0.072 ± 0.000
T 2h	0.062 ± 0.002	0.036 ± 0.004	0.052 ± 0.004	0.046 ± 0.002	0.028 ± 0.002
T 6h	0.026 ± 0.002	0.028 ± 0.002	0.046 ± 0.004	0.040 ± 0.001	0.026 ± 0.002
T 24h	Tr	Tr	Tr	Tr	Tr
T 48h	nd	nd	nd	nd	nd
Flavanones					
NarGE-7-O-GlucSD					
T 0h ^d	0.030 ± 0.001	Tr	Tr	Tr	Tr
T 2h	0.056 ± 0.007	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	nd	nd	nd	nd	nd
T 48h	nd	nd	nd	nd	nd

nd= not detected; Tr=traces. ^a Full compound names are shown in Table S2. ^b Tentatively identified and semiquantified compounds. ^c Compounds derived from colonic fermentation. ^d T0h was assumed to correspond to (poly)phenolic content of pepper samples after *in vitro* gastrointestinal digestion.

Table S5. Phenolic compounds derived from other sources identified and quantified during the 48h colonic fermentation of raw and thermally treated Piquillo pepper. Results are expressed as μmol of (poly)phenolic compound per g of pepper (dry matter) (mean \pm standard deviation, n=3).

Compound ^a	Raw	Grilled	Canned	Microwaved	Fried
3-PrA					
T 0h ^c	0.693 \pm 0.014	0.729 \pm 0.010	0.820 \pm 0.024	0.871 \pm 0.010	0.649 \pm 0.009
T 2h	0.252 \pm 0.020	nd	nd	nd	nd
T 6h	Tr	nd	nd	nd	nd
T 24h	12.544 \pm 1.095	10.110 \pm 0.401	Tr	Tr	29.613 \pm 2.131
T 48h	nd	nd	nd	nd	nd
PhA					
T 0h ^c	1.078 \pm 0.049	1.053 \pm 0.065	1.187 \pm 0.029	1.298 \pm 0.025	0.757 \pm 0.007
T 2h	0.926 \pm 0.064	nd	nd	nd	nd
T 6h	nd	nd	nd	nd	nd
T 24h	40.557 \pm 1.656	17.322 \pm 1.520	34.604 \pm 2.307	67.461 \pm 5.542	127.327 \pm 8.665
T 48h	Tr	Tr	Tr	Tr	5.964 \pm 0.511
4'-OH-PhA^b					
T 0h ^c	nd	nd	nd	nd	nd
T 2h	Tr	Tr	0.864 \pm 0.059	0.504 \pm 0.016	0.243 \pm 0.016
T 6h	nd	nd	7.559 \pm 0.806	3.411 \pm 0.127	2.303 \pm 0.123
T 24h	33.171 \pm 2.416	17.874 \pm 0.462	51.987 \pm 2.614	55.923 \pm 0.073	57.236 \pm 2.687
T 48h	0.642 \pm 0.072	0.801 \pm 0.035	28.229 \pm 2.050	46.817 \pm 3.292	42.275 \pm 2.386

nd= not detected; Tr= traces.^a Full compound names are shown in Table S2. ^b Compounds derived from colonic fermentation. ^c T0h was assumed to correspond to (poly)phenolic content of pepper samples after *in vitro* gastrointestinal digestion.