Supporting Information

Carbonyl-trapping by phenolics and the inhibition of the formation of carcinogenic heterocyclic aromatic amines with the structure of aminoimidazoazaarene in beef patties

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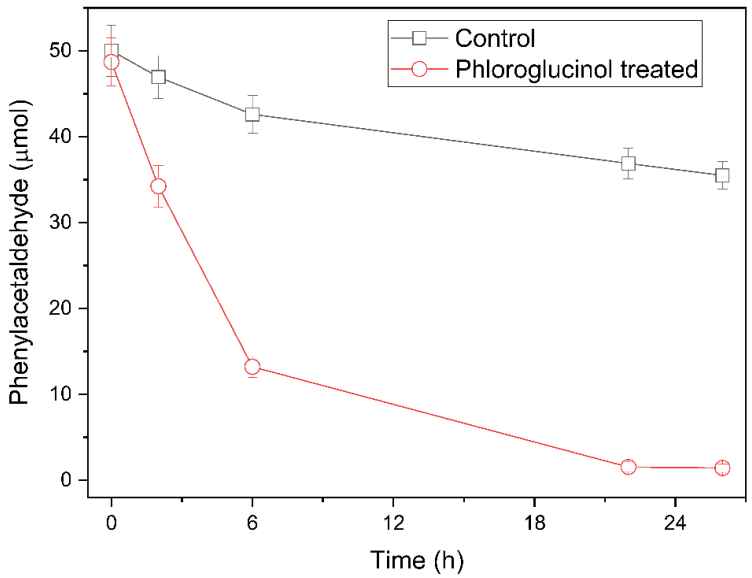


Figure S1. Phenylacetaldehyde disappearance during incubation at 60 ºC in the absence (□) and in the presence (○) of phloroglucinol. Phenylacetaldehyde was determined directly by GC-MS.

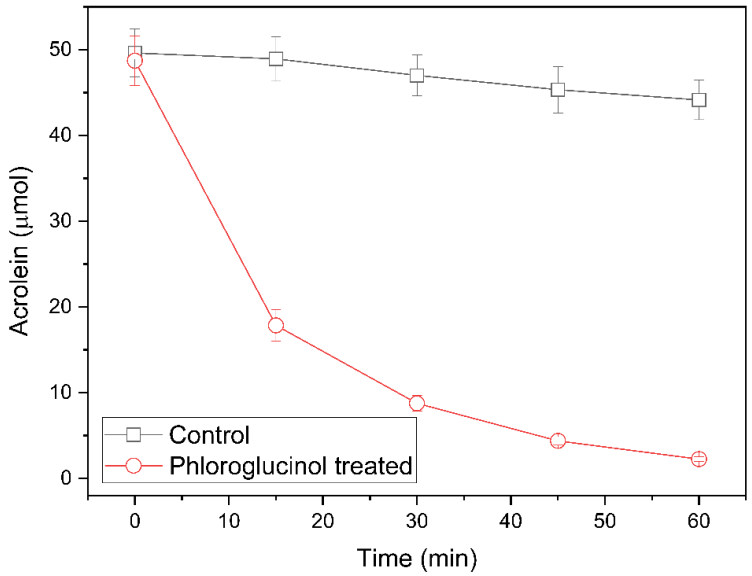


Figure S2. Acrolein disappearance during incubation at 100 ºC in the absence (□) and in the presence (○) of phloroglucinol. Acrolein was determined by GC-MS after derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine.

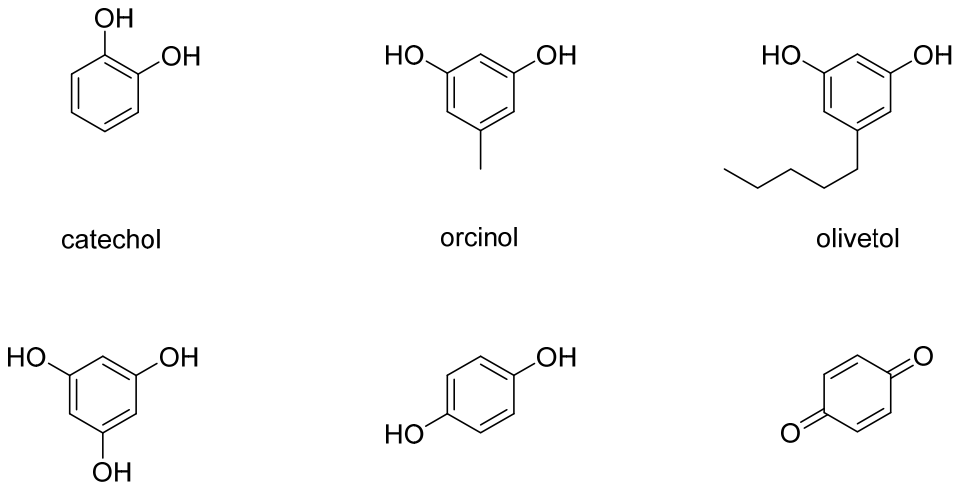


Figure S3. Chemical structures of assayed phenolic compounds.

Table S1

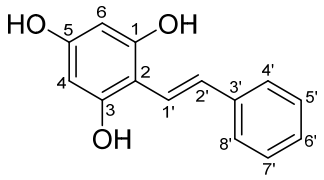
Optimization of MRM transitions for detection of HAAs and carbonyl/phloroglucinol adducts

Compound	Monitored transition	DP	CE	CXP
PhIP	225.021 → 206.900	120	20	6
	225.021 → 210.000	80	40	8
	225.021 → 190.900	120	40	6
MeIQx	214.048 → 199.000	60	40	6
	214.048 → 131.000	60	50	8
	214.048 → 172.000	60	40	6
IQ	**199.020 → 184.000**	80	40	8
	199.020 → 157.000	60	50	8
	199.020 → 129.900	60	50	8
MeIQ	**213.037 → 198.000**	60	40	6
	213.037 → 170.000	60	50	8
	213.037 → 84.900	60	40	6
Adduct **4**	**228.997 → 151.000**	80	20	10
	228.997 → 123.000	80	30	10
	228.997 → 117.000	80	50	10
Adduct **7**	**183.039 → 139.000**	20	20	12
	183.039 → 67.000	20	30	12
	183.039 → 77.000	20	60	12
Adduct **8**	**239.002 → 151.000**	80	30	12
	239.002 → 139.000	80	30	12
	239.002 → 176.900	80	20	12
Adduct **10**	**295.016 → 277.100**	80	20	12
	295.016 → 233.100	80	30	12
	295.016 → 189.000	80	15	12
IS	**195.019 → 137.900**	36	27	32
	195.019 → 110.100	36	31	14
	195.019 → 123.100	36	41	8

Abbreviations: DP, declustering potential; CE, collision energy; CXP, collision cell exit potential. Transition employed for quantification purposes is in bold.

NMR and MS data of compound (4)

2-Styrylbenzene-1,3,5-triol



(**4**)

^{1}H NMR (500 MHz, CD_3OD): δ 5.92 (s, 2H, H4 and H6), 7.13 (tt, 1H, *J* = 1.3 Hz, *J* = 7.5 Hz, H6'), 7.28 (tt, 2H, *J* = 1.3 Hz, *J* = 7.5 Hz, H4' and H8'), 7.41 (d, 1H, *J* = 16.5 Hz, H1'), 7.44 (m, 2H, H5' and H7'), and 7.47 (d, 1H, *J* = 16.5 Hz, H2').

^{13}C NMR (125.7 MHz, CD_3OD): δ 94.35 (C4 and C6), 104.71 (C2), 120.60 (C1'), 125.29 (C5' and C7'), 125.59 (C6'), 127.42 (C2'), 128.02 (C4′ and C8'), 157.30 (C5), and 157.54 (C1 and C3).

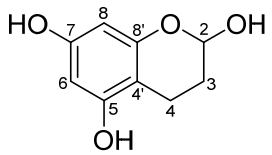
MS, *m/z* (%, ion structure): 228 (100, M^+), 211 (6, M^+ – OH), 150 (15, M^+ – benzene), and 125 (19, phloroglucinol – H).

MS of the trimethylsilyl derivative, *m/z* (%, ion structure): 444 (100, M^+), 429 (15, $M^+ – CH_3$), 371 (5, $M^+ – (CH_3)_3Si$), and 73 (76, $(CH_3)_3Si$).

MS of the acetate derivative, *m/z* (%, ion structure): 354 (8, M^+), 312 (17, $M^+ – CH_2CO$), 270 (29, 312 – CH_2CO), and 228 (100, 270 – CH_2CO).

NMR and MS data of compound (7)

Chromane-2,5,7-triol



(**7**)

^{1}H NMR (500 MHz, CD_3OD): δ 1.89 (m, 2H, H3), 2.61 (m, 2H, H4), 5.39 (dd, 1H, *J* = 2.6 Hz, *J* = 4.8 Hz, H2), 5.80 (d, 1H, *J* = 2.3 Hz, H8), and 5.91 (d, 1H, *J* = 2.3 Hz, H6).

^{13}C NMR (125.7 MHz, CD_3OD): δ 14.97 (C4), 27.32 (C3), 92.09 (C2), 94.73 (C8), 94.79 (C6), 100.93 (C4′), 153.94 (C8’), 155.54 (C5), and 156.18 (C7).

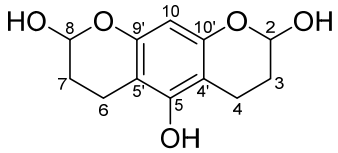
MS, *m/z* (%, ion structure): 182 (36, M^+), 163 (22), 139 (66, $M^+ - C_2H_3O$), and 126 (100, phloroglucinol).

MS of the trimethylsilyl derivative, *m/z* (%, ion structure): 398 (6, M^+), 383 (7, $M^+ - CH_3$), 308 (27, $M^+ - (CH_3)_3SiOH$), and 73 (100, $(CH_3)_3Si$).

MS of the acetate derivative, *m/z* (%, ion structure): 308 (2, M^+), 248 (15, $M^+ - CH_3COOH$), 206 (50, 248 – CH_2CO), and 164 (100, 206 – CH_2CO).

NMR and MS data of compound (8)

3,4,7,8-Tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromene-2,5,8-triol



(**8**)

^{1}H NMR (500 MHz, CD_3OD): δ 1.89 (m, 4H, H3 and H7), 2.61 (m, 4H, H4 and H6), 5.46 (m, 2H, H2 and H8), and 6.13 (s, 1H, H10).

^{13}C NMR (125.7 MHz, CD_3OD): δ 15.2 (C4 and C6), 28.3 (C3 and C7), 92.11 (C2 and C8), 95.01 (C10), 101.75 (C4′ and C5’), 150.59 (C5), and 153.36 (C9’ and C10’).

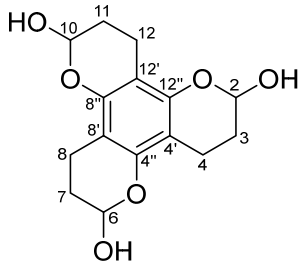
MS, *m/z* (%, ion structure): 238 (44, M^+), 220 (9, $M^+ – H_2O$), 195 (23, $M^+ – C_2H_3O$), 182 (65, chromane-2,5,7-triol), 151 (89, 182 – CH_3O), and 126 (100, phloroglucinol).

MS of the trimethylsilyl derivative, *m/z* (%, ion structure): 454 (11, M^+), 439 (4, $M^+ – CH_3$), 364 (8, $M^+ – (CH_3)_3SiOH$), 338 (14, $M^+ – (CH_3)_3SiOC_2H_3$), 337 (25, 338 – H), 323 (9, 338 – CH_3), 248 (16, 338 – $(CH_3)_3SiOH$), and 73 (100, $(CH_3)_3Si$).

MS of the acetate derivative, *m/z* (%, ion structure): 364 (11, M^+), 305 (34, $M^+ – CH_3COO$), 305 (34, $M^+ – CH_3COOH$), 262 (71, 306 – CH_2CO), 244 (34, 306 – CH_3COOH), 220 (100, 262 – CH_2CO), and 202 (54, 244 – CH_2CO).

NMR and MS data of compound (10)

3,4,7,8,11,12-Hexahydro-2*H*,6*H*,10*H*-dipyrano[2,3-*f*:2',3'-*h*]chromene-2,6,10-triol



(**10**)

^{1}H NMR (500 MHz, CD_3OD): δ 1.89 (m, 6H, H3, H7 and H11), 2.64 (m, 6H, H4, H8, and H12), and 5.45 (m, 3H, H2, H6, and H10).

^{13}C NMR (125.7 MHz, CD_3OD): δ 15.01 and 15.12 (C4, C8, and C12), 27.11 and 27.17 (C3, C7, and C11), 91.99 and 92.07 (C2, C6, and C10), 101.81 and 101.83 (C4', C8', and C12'), 148.32 and 148.42 (C4", C8", and C12").

MS, *m/z* (%, ion structure): 294 (2, M^+), 238 (5, M^+ – acrolein), 182 (4, M^+ – acrolein), and 126 (100, phloroglucinol).

MS of the trimethylsilyl derivative, *m/z* (%, ion structure): 510 (8, M^+), 495 (1, M^+ – CH_3), 394 (11, M^+ – $(CH_3)_3SiOCH{=}CH_2$), 393 (20, M^+ – H), 379 (2, 394 – CH_3), 304 (6, 394 – $(CH_3)_3SiOH$), 278 (7, 394 – $(CH_3)_3SiOCH{=}CH_2$), 263 (7, 278 – CH_3), and 73 (100, $(CH_3)_3Si$).

MS of the acetate derivative, *m/z* (%, ion structure): 420 (7, M^+), 405 (5, M^+ – CH_3), 361 (11, M^+ – CH_3COO), 360 (7, M^+ – CH_3COOH), 318 (8, 360 – CH_2CO), 300 (5, 360 – CH_3COOH), 258 (7, 300 – CH_2CO), 240 (5, 300 – CH_3COOH), and 202 (8, 240 – C_3H_2).