Supporting Information

The Balance of Beneficial and Deleterious Health Effects of Quinones: A Case Study of the Chemical Properties of Genistein and Estrone Quinones

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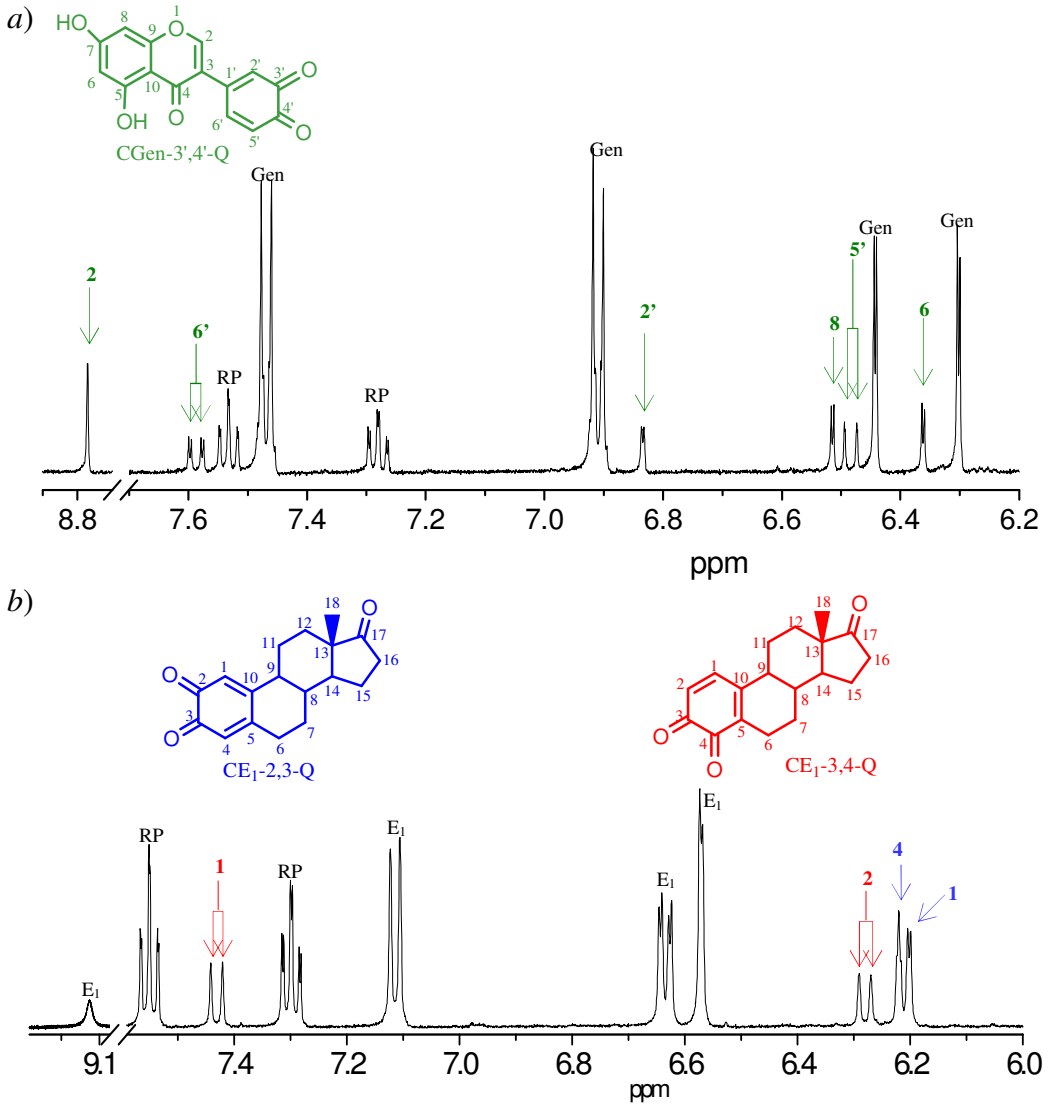
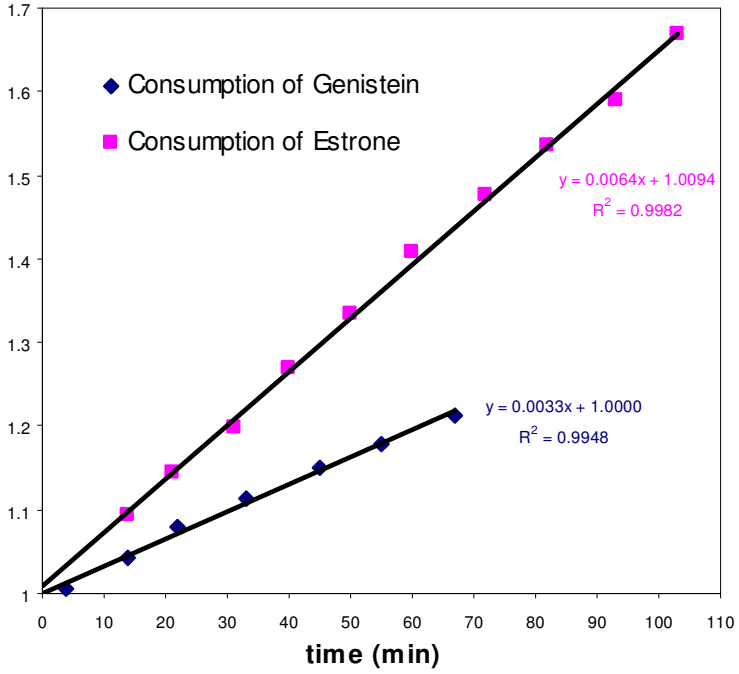


Figure S1. ^{1}H NMR spectra of *a*) Gen + IBX with characteristic ^{1}H of CGen-3′,4′-Q product labeled in green and *b*) E_1 + IBX with characteristic ^{1}H of CE_1-2,3-Q and CE_1-3,4-Q products labeled in red and blue, respectively. Peaks of the reactants Gen or E1 and the reduced product from IBX (RP) in the reaction mixtures were labeled in black. The y axis is intensity.



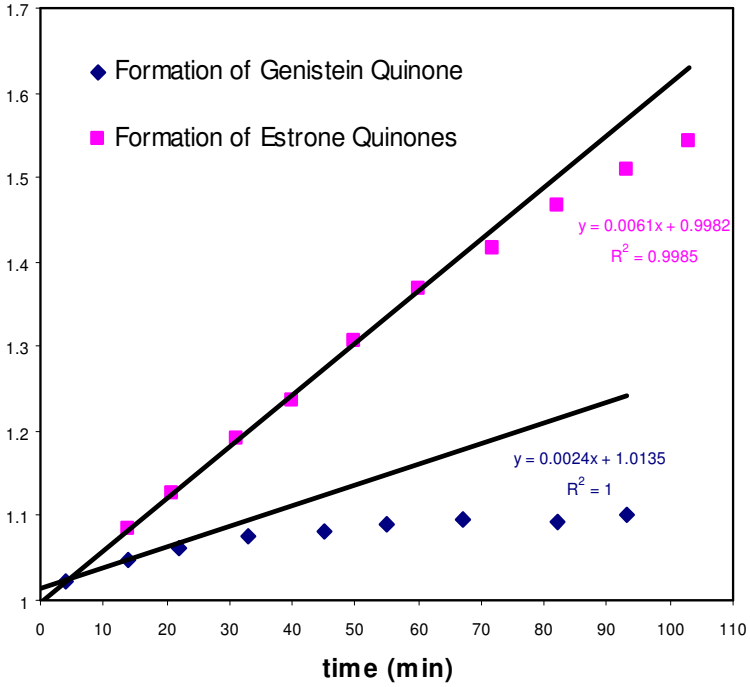


Figure S2. 2nd-Order kinetics of Gen + IBX and E_1 + IBX monitored with NMR. A) Plot of the consumption of Gen and E_1, where $y = \frac{1}{[S]/[S]_0}$ and $[S]$ ≡ concentration of E_1 or Gen at time t and $[S]_0$ ≡ initial concentration of E_1 or Gen. B) Plot of the formation of CGen-3′,4′-Q and CE_1-2,3-Q + CE_1-3,4-Q, where $y = \frac{1}{1-[Q]/[S]_0}$ and $[Q]$ ≡ concentration of the quinone at time t and $[S]_0$ ≡ initial concentration of E_1 or Gen. Red squares represent data for E_1 and blue diamond for Gen. For the formation of E_1, the first six data points were used to calculate rate constant. The formation of CGen-3′,4′-Q deviates from 2nd-order kinetics at ~ 30 min and only the first two data points were used to estimate the rate constant.

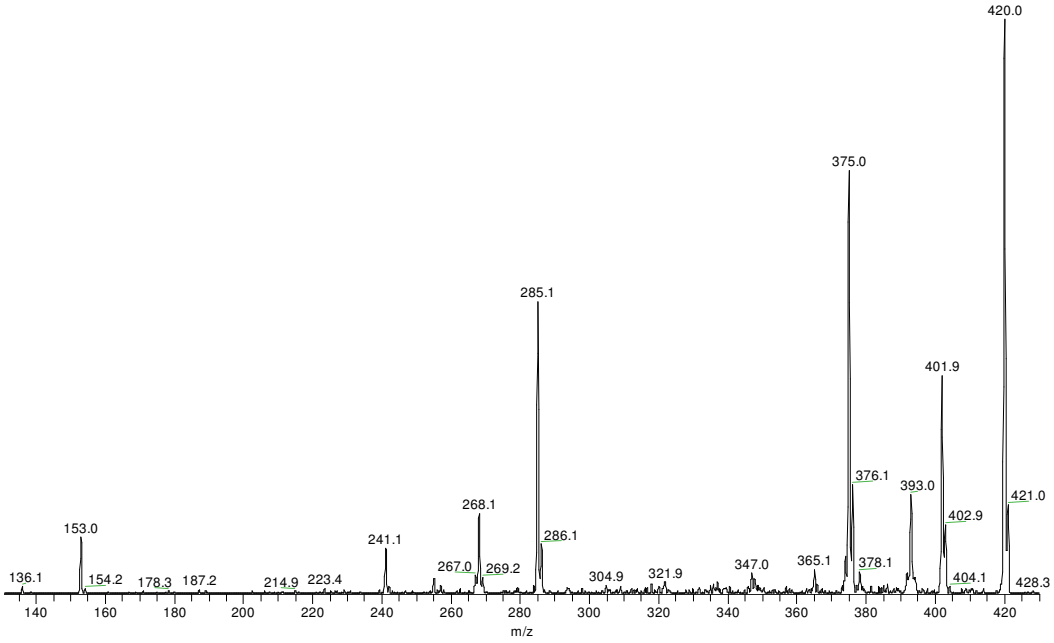
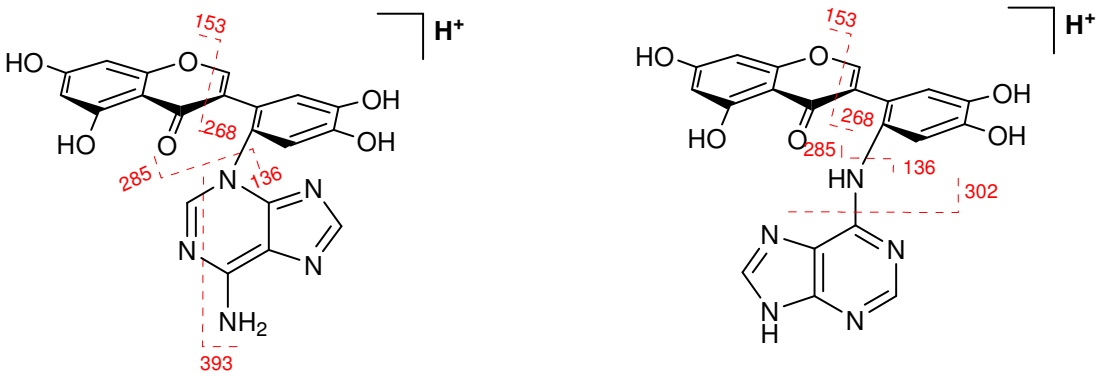


Figure S3. An example of MS/MS product-ion spectrum (y axis is relative abundance) of the CGen-Ade adducts in Figure 4 (t_R = 16.82 min).



[CGen-Ade + H]$^+$
m/z = 420

Figure S4. Representative structures of [CGen-Ade + H]$^+$ adducts. Cleavages shown are in accord with MS/MS observations. One characteristic cleavage of [CGen-Ade + H]$^+$ is C-ring cleavage that produces fragment ions of *m/z* 153 and complementary ion of *m/z* 268.

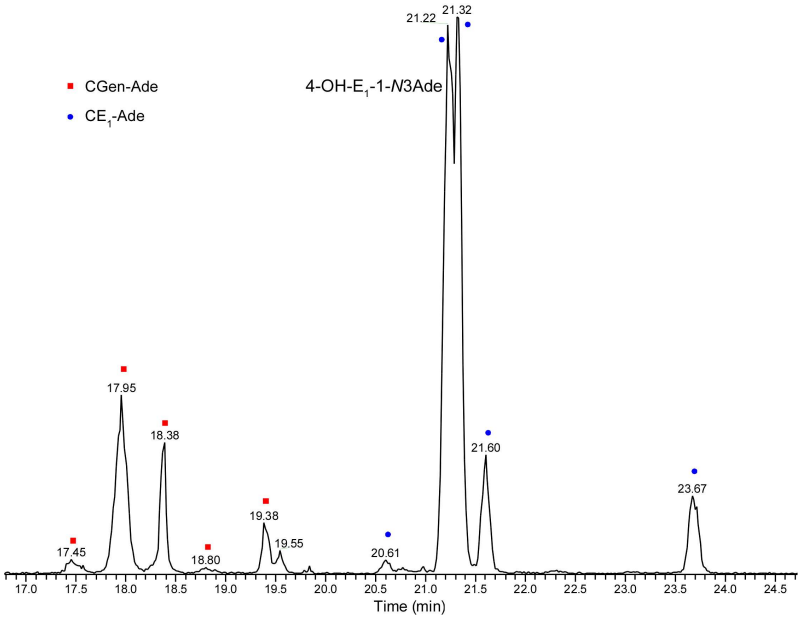


Figure S5. Reconstructed base-peak ion chromatogram (y axis is ion intensity) shows the formation of CGen-Ade and CE_1Q-Ade adducts in DMF. The CGenQ + Ade and CE_1Q + Ade were mixed at 1:1 ratio.

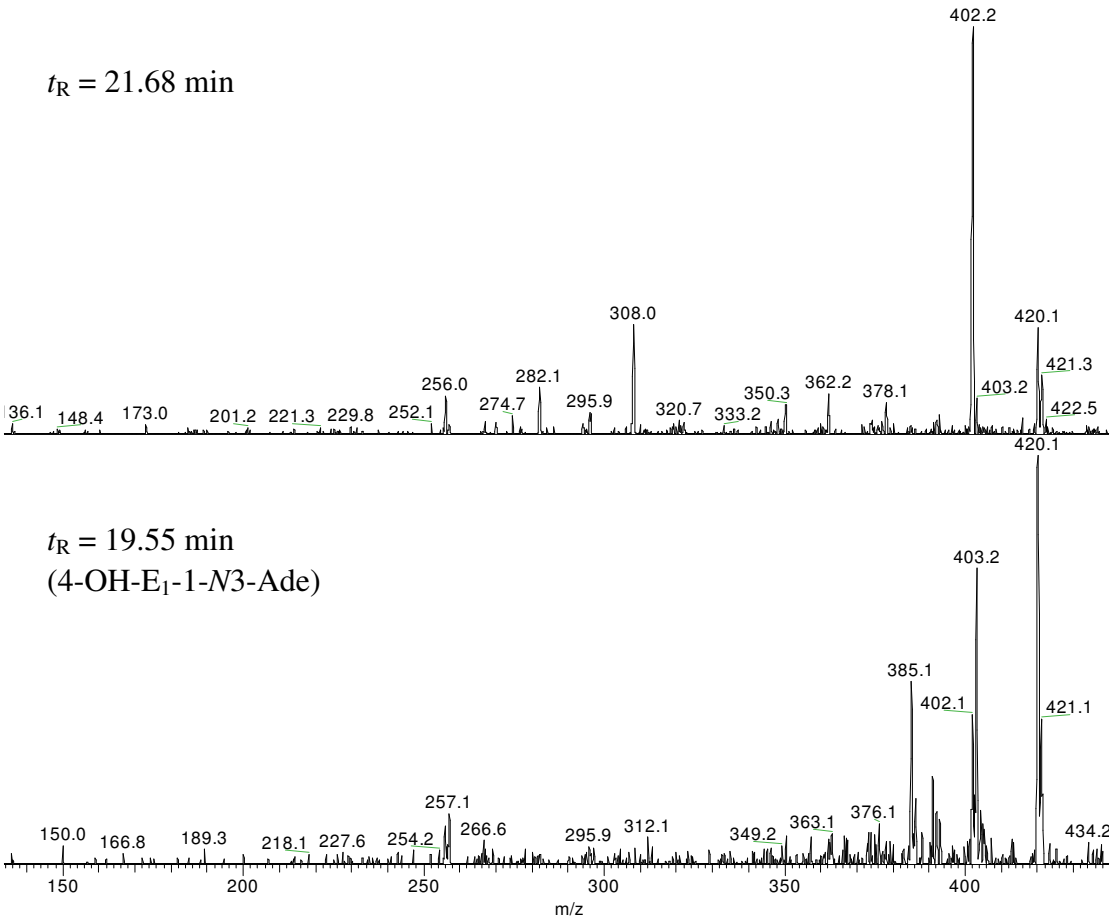


Figure S6. MS/MS Product-ion spectra of the two major CE1-Ade adducts (4-OH-E1-1-*N*3Ade and unknown) identified in the reaction mixture of CE_1Q + calf thymus DNA at pH 7.4, 37 °C. The y axis is relative abundance.

Table S1. Accurate mass measurement of MS/MS product ions of genistein $[C_{15}H_{10}O_5 + H]^+$ and catechol genistein $[C_{15}H_{10}O_6 + H]^+$

Parent	Product	Measured Mass	Theoretical Mass	Deviation (mau)
Genistein	**$C_{15}H_{11}O_5^+$**	**271.0601**	**271.0601**	**0**
	$C_{15}H_9O_4^+$	253.0495	253.0495	0
	$C_{14}H_{11}O_4^+$	243.0652	243.0652	0
	$C_{14}H_{11}O_3^+$	227.0703	227.0703	0
	$C_{14}H_9O_3^+$	225.0546	225.0546	0
	$C_{13}H_{11}O_3^+$	215.0703	215.0703	0
	$C_{13}H_9O_2^+$	197.0597	197.0597	0
	$C_{11}H_7O_3^+$	187.0390	187.0390	0
	$C_{10}H_7O_2^+$	159.0441	159.0441	0
	$C_7H_5O_4^+$	153.0183	153.0183	0
	$C_8H_5O_3^+$	149.0233	149.0233	0
Catechol Genistein	**$C_{15}H_{11}O_6^+$**	**287.0551**	**287.0550**	**+0.1**
	$C_{15}H_9O_5^+$	269.0445	269.0444	+0.1
	$C_{14}H_{11}O_5^+$	259.0602	259.0601	+0.1
	$C_{13}H_7O_6^+$	259.0238	259.0237	+0.1
	$C_{14}H_9O_4^+$	241.0496	241.0495	+0.1
	$C_{13}H_5O_5^+$	241.0137	241.0131	+0.6
	$C_{13}H_{11}O_4^+$	231.0653	231.0652	+0.1
	$C_{12}H_7O_5^+$	231.0289	231.0288	+0.1
	$C_{13}H_9O_3^+$	213.0546	213.0546	0
	$C_{11}H_7O_4^+$	203.0339	203.0339	0
	$C_7H_5O_4^+$	153.0183	153.0183	0

Table S2. Accurate mass measurement for the five catechol genistein adenine $[C_{20}H_{13}N_5O_6 + H]^+$ adducts shown in Figure S5.

Retention time (min)	Measured Mass	Deviation (mau)
17.45	420.0939	0.0
17.95	420.0938	–0.1
18.38	420.0941	+0.2
18.80	420.0937	–0.2
19.38	420.0938	–0.1