Supporting Information

Stability Study and Identification of Degradation Products of Caffeoylgluconic Acid Derivatives from Fructus Euodiae

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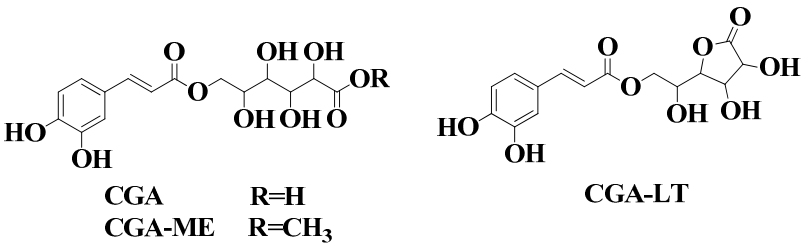

Figure S1. The chemical structural formula of CGA, CGA-ME and CGA-LT.

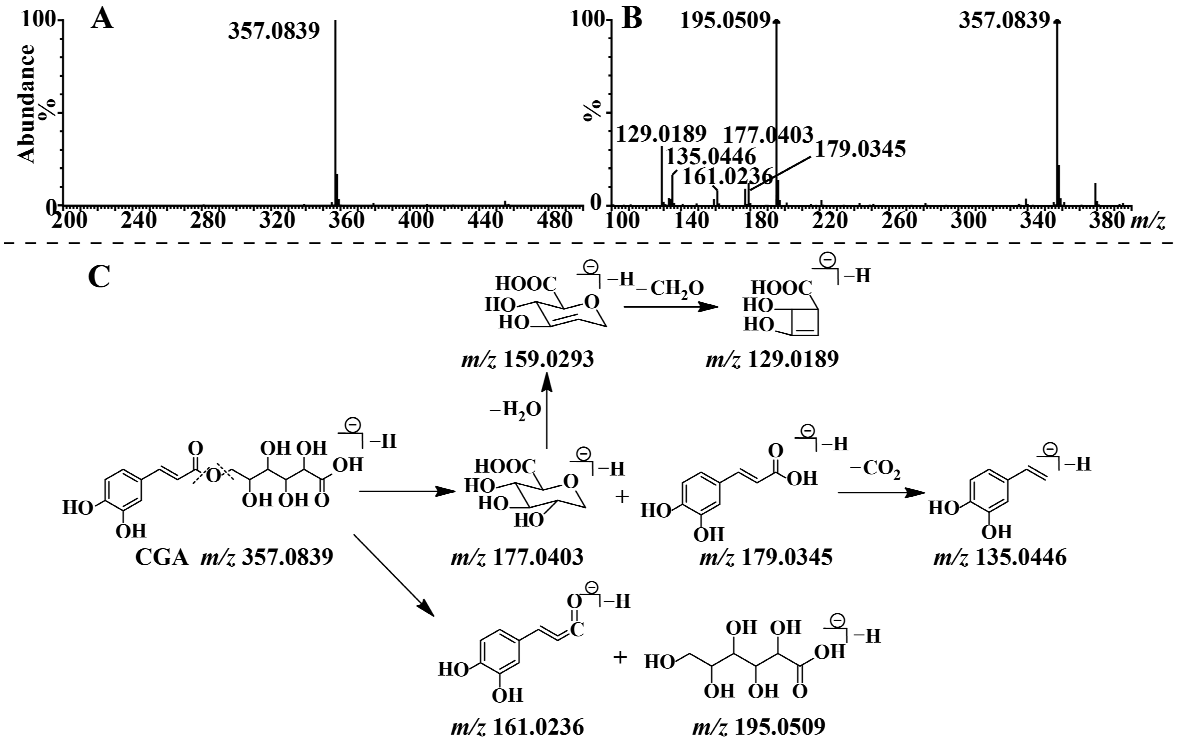

Figure S2. MS (A) and MS^2 (B) spectra, and the proposed fragmentation pattern (C) of CGA.

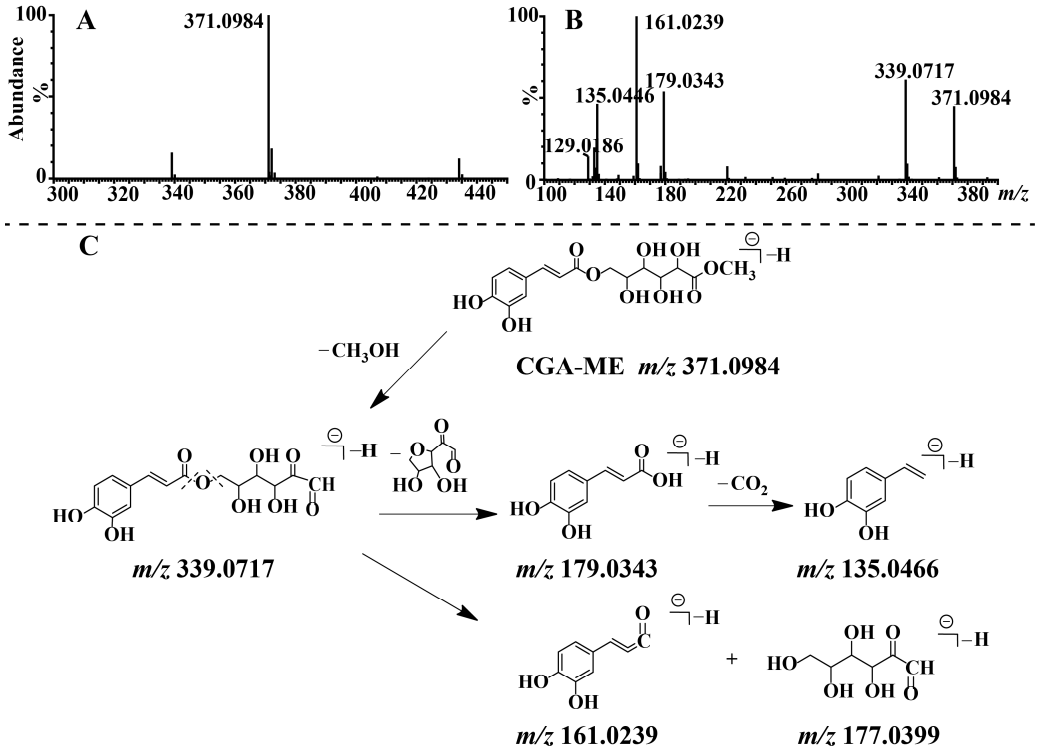

Figure S3. MS (A) and MS^2 (B) spectra, and the proposed fragmentation pattern (C) of CGA-ME.

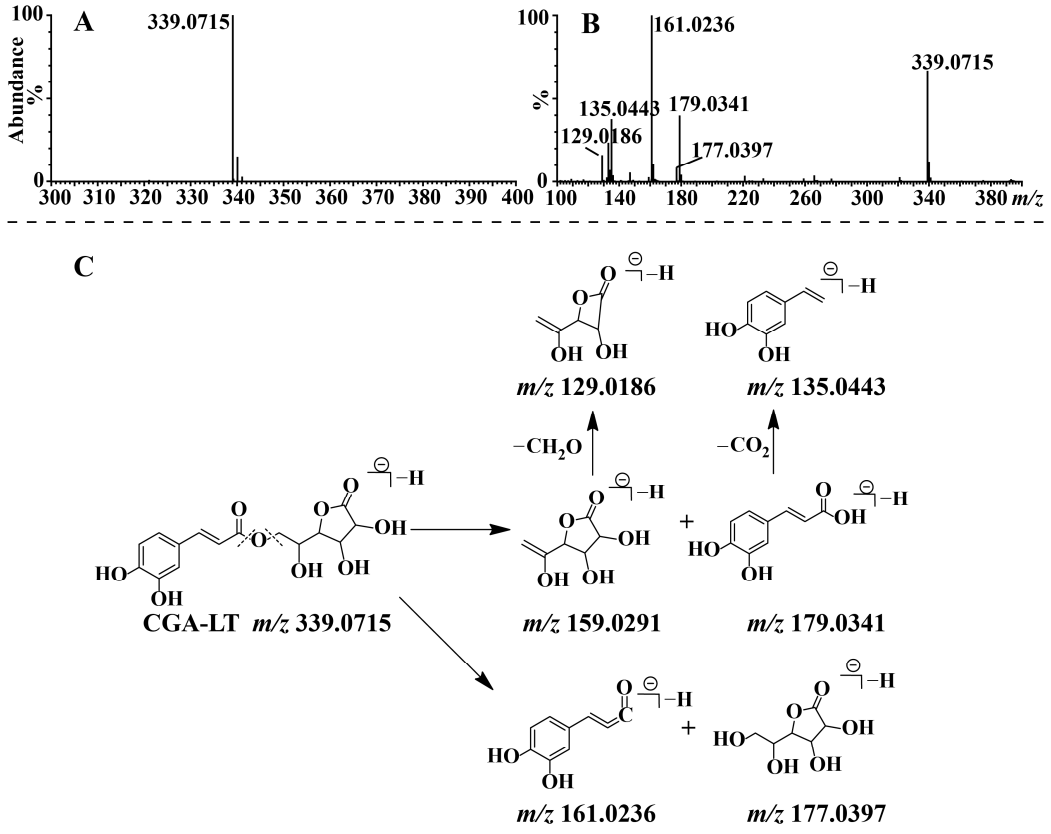

Figure S4. MS (A) and MS^2 (B) spectra, and the proposed fragmentation pattern (C) of CGA-LT.

Table S1. Characterization of the degradation products of CGA, CGA-ME and CGA-LT by UPLC-DAD/ESI-Q-TOF MS.

Compounds	t_R (min)	$[M–H]^-$	MS^2	Identification
CGA–d_1	2.55	357.0820	195.0503 $[M–H–caffeoyl]^-$	Isomer of CGA
			179.0342 $[M–H–gluconic\ acid\ residue]^-$	
			135.0443 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0187 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	
CGA–d_2	2.93	357.0822	195.0504 $[M–H–caffeoyl]^-$	Isomer of CGA
			179.0345 $[M–H–gluconic\ acid\ residue]^-$	
			135.0445 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0188 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	
CGA–d_3	3.12	357.0822	195.0504 $[M–H–caffeoyl]^-$	Isomer of CGA
			179.0343 $[M–H–gluconic\ acid\ residue]^-$	
			135.0444 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0189 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	
CGA–d_4	3.87	357.0825	195.0506 $[M–H–caffeoyl]^-$	Isomer of CGA
			179.0343 $[M–H–gluconic\ acid\ residue]^-$	
			135.0445 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0188 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	
CGA	5.70	357.0839	195.0509 $[M–H–caffeoyl]^-$	CGA
			179.0345 $[M–H–gluconic\ acid\ residue]^-$	
			135.0446 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0189 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	
CGA-ME → CGA	4.90	357.0819	195.0509 $[M–H–caffeoyl]^-$	CGA
			179.0341 $[M–H–gluconic\ acid\ residue]^-$	
			135.0443 $[M–H–gluconic\ acid\ residue–CO_2]^-$	
			129.0186 $[M–H–caffeoyl–2H_2O–CH_2O]^-$	

CGA-ME–d_1	6.33	371.0988	339.0713 [M–H–CH_3OH]$^-$ 179.0343 [M–H–methyl gluconic acid residue]$^-$ 177.0398 [M–H–CH_3OH–caffeoyl]$^-$ 161.0237 [M–H–methyl gluconic acid]$^-$ 135.0445 [M–H–methyl gluconic acid residue–CO_2]$^-$	Isomer of CGA-ME
CGA-LT–d_1	6.58	339.0714	–	Isomer of CGA-LT
CGA-ME–d_2	6.89	179.0342	–	Caffeic acid
CGA-LT–d_2	8.55	339.0712	179.0341 [M–H–glucono-γ-lactone residue]$^-$ 177.0397 [M–H–Caffeoyl]$^-$ 161.0236 [M–H–glucono-γ-lactone]$^-$ 135.0443 [M–H–glucono-γ-lactone residue–CO_2]$^-$ 129.0185 [M–H–caffeic acid–CH_2O]$^-$	Isomer of CGA-LT
CGA-ME	9.09	371.0984	339.0717 [M–H–CH_3OH]$^-$ 179.0343 [M–H–methyl gluconic acid residue]$^-$ 177.0399 [M–H–CH_3OH–caffeoyl]$^-$ 161.0239 [M–H–methyl gluconic acid]$^-$ 135.0446 [M–H–methyl gluconic acid residue–CO_2]$^-$	CGA-ME
CGA-ME → CGA-LT	13.07	339.0715	179.0342 [M–H–glucono-γ-lactone residue]$^-$ 177.0399 [M–H–caffeoyl]$^-$ 161.0237 [M–H–glucono-γ-lactone]$^-$ 135.0443 [M–H–glucono-γ-lactone residue–CO_2]$^-$ 129.0185 [M–H–caffeic acid–CH_2O]$^-$	CGA-LT

CGA-LT → CGA	4.90	357.0838	195.0505 [M–H–caffeoyl]$^-$ 179.0341 [M–H–gluconic acid residue]$^-$ 135.0443 [M–H–gluconic acid residue–CO_2]$^-$ 129.0186 [M–H–caffeoyl–$2H_2O$–CH_2O]$^-$	CGA
CGA-LT–d_1	6.56	339.0728	179.0345 [M–H–glucono-γ-lactone residue]$^-$ 177.0399 [M–H–caffeoyl]$^-$ 161.0238 [M–H–glucono-γ-lactone]$^-$ 135.0445 [M–H–glucono-γ-lactone residue–CO_2]$^-$ 129.0186 [M–H–caffeic acid–CH_2O]$^-$	Isomer of CGA-LT
CGA-LT–d_2	8.50	339.0710	179.0340 [M–H–glucono-γ-lactone residue]$^-$ 177.0395 [M–H–caffeoyl]$^-$ 161.0234 [M–H–glucono-γ-lactone]$^-$ 135.0442 [M–H–glucono-γ-lactone residue–CO_2]$^-$ 129.0184 [M–H–caffeic acid–CH_2O]$^-$	Isomer of CGA-LT
CGA-LT	13.01	339.0715	179.0341 [M–H–glucono-γ-lactone residue]$^-$ 177.0397 [M–H–caffeoyl]$^-$ 161.0236 [M–H–glucono-γ-lactone]$^-$ 135.0443 [M–H–glucono-γ-lactone residue–CO_2]$^-$ 129.0186 [M–H–caffeic acid–CH_2O]$^-$	CGA-LT