SUPPLEMENTARY MATERIAL

Table S1. Tentatively identified compounds, abbreviation, retention time, m/z, molecular formula, error and fragments information.

Compound	Abbreviation	TR (min)	m/z	Molecular formula	Error (ppm)	Fragments information
Quinic acid	QuiAc	2.1	191.0568	$C_7 H_{12} O_6$	-3.43	191.0572, 127.0408, 109.0282
3.4-Dihydroxyphenylglycol	DiHyGli	4.2	169.0514	$C_8 H_{10} O_4$	-4.61	123.0453, 122.0372, 108.0235
Vanillic acid	Van	7.8	167.0359	$C_8 H_8 O_4$	-5.18	123.0455, 108.0218, 109.0296, 122.0365
Hydroxytyrosol	Hyty	8.6	153.0566	$C_8 H_{10} O_3$	-5.71	123.0455, 153.056
3-(formylpropenyl) pentanoic acid	ForP	9.8	199.0622	$C_9 H_{12} O_5$	-4.92	111.0819, 199.0615, 155.0711, 111.009
Tyrosol	Ty	9.9	137.061	$C_8 H_{10} O_2$	-1.43	
Elenolic acid isomer 1	EA 1	10.5	241.0729	$C_{11} H_{14} O_6$	-4.53	139.0040, 127.0402, 101.0247, 111.0091
Elenolic acid isomer 2	EA 2	10.7	241.0732	$C_{11} H_{14} O_6$	-5.74	139.0037, 101.0244, 127.0400, 111.0088
Decarboxymethyl dialdehydic acid elenolic acid	DEDA	11.9	183.0672	$C_9 H_{12} O_4$	-5.03	
Hydroxydecarboxymethyl oleuropein aglycone isomer 1	HyDec Ol Ag 1	12.8	671.2358	$C_{17} H_{20} O_7$	-3.22	151.0405, 335.1142
Hydroxyoleuropein aglycone isomer 1	Hy Ol Ag 1	13.5	393.1200	$C_{19} H_{22} O_9$	-2.06	151.0407, 123.0455, 139.0044
Trimethoxyphenylacetic acid	TMP-Ac	14.5	225.0782	$C_{11} H_{14} O_5$	-5.56	101.0245, 123.0450
Hydroxytyrosol acetate	Hyty-Ac	15.6	195.0669	$C_{10} H_{12} O_4$	-3.08	101.0244, 135.0453, 121.0292
Hydroxyelenolic acid	Hy-EA	17.4	257.068	$C_{11} H_{14} O_7$	-4.82	137.0606, 109.0658, 181.0505
Syringaresinol	Syr	17.5	417.1555	$C_{22} H_{26} O_8$	-0.02	
Pinoresinol	Pin	18.2	357.1344	$C_{20}H_{22}O_6$	-0.11	

Hydroxydecarboxymethyl oleuropein aglycone isomer 2	Hy-D-Ol-Agl 2	18.5	335.1149	$C_{17}H_{20}O_7$	-3.61	111.0816, 199.0617, 155.0717
Acetoxypinoresinol	Ac-Pin	18.6	415.1398	$C_{22}H_{24}O_8$	0.1	
Hydroxyoleuropein aglycone isomer 1	Hy-Ol-Ag 1	20.5	393.1206	$C_{19}H_{22}O_9$	-3.51	151.0396, 111.0083, 101.0244, 139.0036
Ligstroside aglycone isomer 1	Li-Ag 1	20.9	361.1306	$C_{19}H_{22}O_7$	-3.65	
Methyloleuropein aglycone isomer 1	Me-Ol-Ag 1	21.1	391.1409	$C_{20}H_{24}O_8$	-2.6	
Ligstroside aglycone isomer 2	Li-Ag 2	21.3	361.1307	$C_{19}H_{22}O_7$	-3.93	101.0240, 291.0879, 111.0089
Methyloleuropein aglycone isomer 2	Me-Ol-Ag 2	21.6	391.1411	$C_{20}H_{24}O_8$	-2.91	111.0095, 139.0036, 115.0401
Methyloleuropein aglycone isomer 3	Me-Ol-Ag 3	21.8	391.1407	$C_{20}H_{24}O_8$	-2.27	
Hydroxydecarboxymethyl ligstroside aglycone	Hy-D-Li-Agl	22.0	319.1199	$C_{17}H_{20}O_6$	-3.33	199.0613, 111.0089, 111.0817, 155.0713, 181.0507
Ligstroside aglycone isomer 3	Li-Ag 3	22.2	361.1314	$C_{19}H_{22}O_7$	-5.86	101.0246, 291.0879, 127.0403, 111.0088
Hydroxyoleuropein aglycone isomer 2	Hy-Ol-Ag 2	22.3	393.1206	$C_{19}H_{22}O_9$	-3.58	
Ligstroside aglycone isomer 4	Li-Ag 4	22.5	361.131	$C_{19}H_{22}O_7$	-4.4	101.0247, 291.0886, 127.0405, 111.0090, 292.0917
Methyloleuropein aglycone isomer 4	Me-Ol-Ag 4	22.6	391.1407	$C_{20}H_{24}O_8$	-2.05	
Oleuropein aglycone isomer 1	Ol-Ag 1	23.6	751.2268	$C_{19}H_{20}O_8$	-3.48	111.0090, 149.0245, 139.0405, 101.0246
Hydroxyoleuropein aglycone isomer 3	Hy-D-Ag 3	24.8	393.1206	$C_{19}H_{22}O_9$	-3.59	
Oleuropein aglycone isomer 2	Ol-Ag 2	25.0	377.1256	$C_{19}H_{22}O_8$	-3.65	111.0090, 149.0245, 139.0405, 101.0246
Luteolin	Lut	25.5	285.0421	$C_{15}H_{10}O_6$	-5.39	133.0293, 285.0402, 151.0033
Ligstroside aglycone isomer 5	Li-Ag 5	26.0	361.1308	$C_{19}H_{22}O_7$	-3.79	101.0246, 291.0878, 127.0400, 111.0090

Methyloleuropein aglycone isomer 5	Me-Ol-Ag 5	26.1	391.1414	$C_{20}H_{24}O_8$	-3.81	111.0086, 139.0036, 139.0399, 115.0397, 141.0556
Oleuropein aglycone isomer 3	Ol-Ag 3	26.2	377.1257	$C_{19}H_{22}O_8$	-3.75	111.009, 101.0247, 139.0039, 149.0245, 139.0401
Ligstroside aglycone isomer 6	Li-Ag 6	26.3	361.1305	$C_{19}H_{22}O_7$	-3.05	101.0249, 291.0878, 127.0404, 111.0091, 292.0910
Elenolic decarboxymethyl dialdehydic acid acetal	DEDA-Ac	26.4	365.1618	$C_{19}H_{26}O_7$	-3.28	
Methyloleuropein aglycone isomer 6	Me-Ol-Ag 6	26.5	391.1409	$C_{20}H_{24}O_8$	-2.4	111.0086, 139.0036, 115.0397, 141.0556
Apigenin	Api	26.7	269.0466	$C_{15}H_{10}O_5$	-3.71	117.0348, 269.0458, 151.0038, 149.0245
Oleuropein aglycone isomer 4	Ol-Ag 4	26.7	377.1257	$C_{19}H_{22}O_8$	-3.72	111.0086, 139.0402, 139.0036, 101.0245, 149.0243
Ligstroside aglycone isomer 7	Li-Ag 7	27.0	361.1311	$C_{19}H_{22}O_7$	-5.04	

Table S2. Calibration parameters for standards used in the quantification.

Compound	Calibration range (μg mL^{-1})	Calibration curve	R^2	LOD (μg mL^{-1})	LOQ (μg mL^{-1})
BenAc	1–40	$y = -59.9 x^2 + 7467.6 x + 11136$	0.9962	0.55	1.64
Hyty	1–150	$y = -242 x^2 + 97878 x + 80667$	0.9987	0.07	0.20
Ty	1–40	$y = 74.6 x^2 + 32965 x - 10370$	0.9989	0.14	0.42
Lut	1–40	$y = -3209.1 x^2 + 355617 x + 401034$	0.9969	0.02	0.06
Ol	1–150	$y = -237.4 x^2 + 74636 x + 264040$	0.9943	0.05	0.16
Pin	1–40	$y = -661.7 x^2 + 104606 x + 5319.7$	0.9990	0.02	0.06
QuinAc	1–40	$y = -417.1 x^2 + 123852 x + 21480$	0.9963	0.04	0.12
Van	1–40	$y = -607.2 x^2 + 64345 x + 39052$	0.9960	0.06	0.19

BenAc, benzylic acid; Hyty, hydroxytyrosol; Ty, tyrosol; Lut, luteoline; Ol, oleuropeine; Pin, pinoresinol; QuinAc, quinic acid; Van, vanillic acid; LOD, limit of detection; LOQ, limit of quantification.