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SUPPLEMENTARY MATERIAL

Target and suspect HRMS metabolomics for the determination of functional ingredients in 13 varieties of olive leaves and drupes from Greece

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Table S1. Olive leaves and drupes varieties and geographical origin

Variety	Geographical Origin	Sample	
		Leaf	**Drupe**
		Sample no	*Sample no*
Koroneiki	Naxos (Melanes)	1F, 1F2	1K
Throumbolia	Naxos (Melanes)	2F, 2F2	2K
Konservolia	Naxos (Melanes)	3F, 3F2	3K
Koutsourelia	Aetolia-Acarnania (Agrinio)	4F, 4F2	4K
Konservolia	Aetolia-Acarnania (Agrinio)	5F, 5F2	5K
Kalamon	Aetolia-Acarnania (Agrinio)	6F, 6F2	-
Petrolia	Serres (Skoutari)	7F, 7F1, 7F2	-
Amigdalolia	Attica (Votanikos)	8F, 8F2	-
Kalamon	Attica (Votanikos)	9F, 9F2	-
Konservolia	Attica (Votanikos)	10F, 10F2	-
Koroneiki	Attica (Votanikos)	11F, 11F2	11K
Koroneiki	Messenia (Kalamata)	12F	-
Kalamon	Messenia (Kalamata)	13F	-
Megaritiki	Attica (Aspropyrgos)	14F	-
Megaritiki	Attica (Sounio)	15F	15K
Megaritiki	Attica (Megara)	16F	16K
Mastoeidis	Laconia (Sparti)	17F, 17F2	17K
Agouromanakolia	Laconia (Sparti)	18F, 18F2	18K
Agrilia	Laconia (Sparti)	19F, 19F2	19K
Agouromanakolia	Arcadia (Kynouria)	20F	20K
Megaritiki	Boeotia (Dilesi)	21F	21K
Koroneiki	Arcadia (Kynouria)	22F	22K
Koroneiki	Boeotia (Dilesi)	23F	23K
Agrilia	Lesvos (Komi)	24F, 24F1, 24F2	-
Adramitiani	Lesvos (Kalloni)	25F, 25F1, 25F2	-
Kolovi	Lesvos (Palaiohori)	26F, 26F2	-
Kolovi	Lesvos (Moria)	27F	-

Table S2. Quality Control results

Compound	%RSD of Peak Area n=11	%RSD of t_R (min) n=11	Δm (±error, mDa) n=11
Oleuropein	0.53	0.05	-0.08
Tyrosol	0.48	0.05	0.03
Hydroxytyrosol	0.61	0.06	0.10

Table S3. Target list

Compound	**Molecular Formula**
Phenolic acids	
Caffeic acid	$C_9H_8O_4$
Ferulic acid	$C_{10}H_{10}O_4$
Gallic acid	$C_7H_6O_5$
Homovanillic acid	$C_9H_{10}O_4$
p-Coumaric acid	$C_9H_8O_3$
Syringic acid	$C_9H_{10}O_5$
Phenolic alcohols	
Hydroxytyrosol	$C_8H_{10}O_3$
Tyrosol	$C_8H_{10}O_2$
Phenolic aldehydes	
Vanillin	$C_8H_8O_3$
Flavonoids	
Apigenin	$C_{15}H_{10}O_5$
Epicatechin	$C_{15}H_{14}O_6$
Luteolin	$C_{15}H_{10}O_6$
Quercetin	$C_{15}H_{10}O_7$
Secoiridoids	
Oleuropein	$C_{25}H_{32}O_{13}$
Lignans	
Pinoresinol	$C_{20}H_{22}O_6$

Table S4. Suspect list

Compound	Molecular Formula	SMILES
Phenolic acids and derivatives		
2,5-Dihydroxybenzoic acid (Gentisic acid)	$C_7H_6O_4$	OC(=O)C1=CC(O)=CC=C1O
3,4-Dihydroxybenzoic acid (Protocatechuic acid)	$C_7H_6O_4$	OC(=O)C1=CC(O)=C(O)C=C1
Hellicoside	$C_{29}H_{36}O_{17}$	c1cc(c(cc1/C=C/C(=O)O[C@@H]2[C@H](O[C@H]([C@@H]([C@H]2O[C@H]3[C@@H]([C@H]([C@@H]([C@H](O3)CO)O)O)O)O)OC[C@H](c4ccc(c(c4)O)O)O)CO)O)O
4-Hydroxybenzoic acid	$C_7H_6O_3$	OC(=O)C1=CC=C(O)C=C1
4-Hydroxyphenylacetic acid	$C_8H_8O_3$	OC(C(O)=O)C1=CC=CC=C1
Rosmarinic acid	$C_{18}H_{16}O_8$	c1cc(c(cc1C[C@H](C(=O)O)OC(=O)/C=C/c2ccc(c(c2)O)O)O)O
Vanillic acid	$C_8H_8O_4$	COc1cc(ccc1O)C(=O)O
Verbascoside	$C_{29}H_{36}O_{15}$	CC1OC(OC2C(O)C(OCCC3=CC=C(O)C(O)=C3)OC(CO)C2OC(=O)C=CC2=CC=C(O)C(O)=C2)C(O)C(O)C1O
Phenolic alcohols and derivatives		
Calceolarioside	$C_{23}H_{26}O_{11}$	OC[C@H]1O[C@@H](OCCC2=CC=C(O)C(O)=C2)[C@H](O)[C@@H](O)[C@@H]1OC(=O)\C=C\C1=CC(O)=C(O)C=C1
Homovanillyl alcohol	$C_9H_{12}O_3$	COC1=CC(CCO)=CC=C1O
Hydroxytyrosol acetate	$C_{10}H_{12}O_4$	CC(=O)OCCC1=CC(O)=C(O)C=C1
Hydroxytyrosol glucoside	$C_{14}H_{20}O_8$	OC[C@H]1O[C@@H](OCCC2=CC(O)=C(O)C=C2)[C@H](O)[C@@H](O)[C@@H]1O
Tyrosol glucoside (Salidroside)	$C_{14}H_{20}O_7$	[H][C@]1(CO)O[C@@]([H])(OCCC2=CC=C(O)C=C2)[C@]([H])(O)[C@@]([H])(O)[C@]1([H])O

Compound	Molecular Formula	SMILES
		Flavonoids
Apigenin-7-O-glucoside	$C_{21}H_{20}O_{10}$	OC[C@H]1O[C@@H](OC2=CC(O)=C3C(=O)C=C(OC3=C2)C2=CC=C(O)C=C2)[C@H](O)[C@@H](O)[C@@H]1O
Chrysoeriol (Luteolin 3'-methyl ether)	$C_{16}H_{12}O_6$	COC1=CC(=CC=C1O)C1=CC(=O)C2=C(O)C=C(O)C=C2O1
Diosmetin	$C_{16}H_{12}O_6$	COC1=CC=C(C=C1O)C1=CC(=O)C2=C(O)C=C(O)C=C2O1
Diosmin	$C_{28}H_{32}O_{15}$	COC1=CC=C(C=C1O)C1=CC(=O)C2=C(O)C=C(O[C@@H]3O[C@H](CO[C@@H]4O[C@@H](C)[C@H](O)[C@@H](O)[C@H]4O)[C@@H](O)[C@H](O)[C@H]3O)C=C2O1
Fustin	$C_{15}H_{12}O_6$	c1cc(c(cc1[C@@H]2[C@H](C(=O)c3ccc(cc3O2)O)O)O)O
Gallocatechin	$C_{15}H_{14}O_7$	O[C@@H]1CC2=C(O)C=C(O)C=C2O[C@H]1C1=CC(O)=C(O)C(O)=C1
Luteolin-7-O-glucoside	$C_{21}H_{20}O_{11}$	OC[C@@H](O)[C@H]1O[C@@H](OC2=C(OC3=CC(O)=CC(O)=C3C2=O)C2=CC(O)=C(O)C=C2)[C@H](O)[C@H]1O
Luteolin-7,4′-O-diglucoside	$C_{27}H_{30}O_{16}$	OC[C@@H]1O[C@@H](OC2=CC(O)=C3C(=O)C=C(OC3=C2)C2=CC(O[C@@H]3O[C@@H](CO)[C@H](O)[C@@H](O)[C@@H]3O)=C(O)C=C2)[C@@H](O)[C@H](O)[C@H]1O
Naringenin	$C_{15}H_{12}O_5$	c1cc(ccc1[C@@H]2CC(=O)c3c(cc(cc3O2)O)O)O
Quercetin-3-O-glucoside	$C_{21}H_{20}O_{12}$	OC[C@@H](O)[C@H]1O[C@@H](OC2=C(OC3=CC(O)=CC(O)=C3C2=O)C2=CC(O)=C(O)C=C2)[C@H](O)[C@H]1O
Quercetin-3-O-rutinoside (Rutin)	$C_{27}H_{30}O_{16}$	CC1OC(OCC2OC(OC3=C(OC4=CC(O)=CC(O)=C4C3=O)C3=CC=C(O)C(O)=C3)C(O)C(O)C2O)C(O)C(O)C1O
Taxifolin	$C_{15}H_{12}O_7$	OC1C(OC2=CC(O)=CC(O)=C2C1=O)C1=CC=C(O)C(O)=C1

Compound	Molecular Formula	SMILES
Vicenin-2	$C_{27}H_{30}O_{15}$	c1cc(ccc1c2cc(=O)c3c(c(c(c(c3o2)[C@H]4[C@@H]([C@H]([C@@H]([C@H](O4)CO)O)O)O)O)[C@H]5[C@@H]([C@H]([C@@H]([C@H](O5)CO)O)O)O)O)O
		Secoiridoids
Decarboxymethyl ligstroside aglycone (Oleocanthal)	$C_{17}H_{20}O_5$	C\C=C(\C=O)[C@@H](CC=O)CC(=O)OCCC1=CC=C(O)C=C1
Decarboxymethyl oleuropein aglycone (Oleacein)	$C_{17}H_{20}O_6$	C\C=C(\C=O)[C@@H](CC=O)CC(=O)OCCC1=CC(O)=C(O)C=C1
Demethyl oleuropein	$C_{24}H_{30}O_{13}$	C\C=C1\[C@H](O[C@@H]2O[C@H](CO)[C@@H](O)[C@H](O)[C@H]2O)OC=C([C@H]1CC(=O)OCCC1=CC=C(O)C(O)=C1)C(O)=O
Fraxamoside	$C_{25}H_{30}O_{13}$	[H][C@@]12CC(=O)OC[C@H](OC[C@H]3O[C@@H](O[C@H](OC=C1C(=O)OC)\C2=C\C)[C@H](O)[C@@H](O)[C@@H]3O)C1=CC(O)=C(O)C=C1
10-Hydroxy-10-Methyl oleuropein aglycone	$C_{20}H_{24}O_9$	COC(=O)C1=CO[C@@H](O)\C(=C/C(C)O)[C@@H]1CC(=O)OCCC1=CC(O)=C(O)C=C1
10-Hydroxy decarboxymethyl oleuropein aglycone	$C_{17}H_{20}O_7$	[H]C(O)\C=C1\C(O)OC=C[C@H]1CC(=O)OCCC1=CC(O)=C(O
10-Hydroxy oleuropein aglycone	$C_{19}H_{22}O_9$	[H]C(O)\C=C1/[C@H](O)OC=C([C@H]1CC(=O)OCCC1=CC(O)=C(O)C=C1)C(=O)OC
Ligstroside	$C_{25}H_{32}O_{12}$	CC1OC(OC2C(O)C(OCCC3=CC=C(O)C(O)=C3)OC(CO)C2OC(=O)C=CC2=CC=C(O)C(O)=C2)C(O)C(O)C1O
Ligstroside aglycone	$C_{19}H_{22}O_7$	COC(=O)C1=CO[C@@H](O)\C(=C\C)[C@@H]1CC(=O)OCCC1=CC=C(O)C=C1
Nuzhenide	$C_{31}H_{42}O_{17}$	COC(=O)C1=CO[C@@H](O[C@@H]2O[C@H](CO)[C@@H](O)[C@H](O)[C@H]2O)\C(=C/C)C1CC(=O)OC[C@@H]1O[C@H](OCCC2=CC=C(O)C=C2)[C@@H](O)[C@H](O)[C@H]1O

Compound	Molecular Formula	SMILES
Oleoside	$C_{16}H_{22}O_{11}$	[H][C@]1(CO)O[C@@]([H])(O[C@]2([H])OC=C(C(O)=O)[C@@]([H])(CC(O)=O)\C2=C/C)[C@]([H])(O)[C@@]([H])(O)[C@]1([H])O
Oleuropein aglycone	$C_{19}H_{22}O_8$	COC(=O)C1=CO[C@@H](O)\C(=C\C)[C@@H]1CC(=O)OCCC1=CC(O)=C(O)C=C1
Secologanoside	$C_{16}H_{22}O_{11}$	OC[C@H]1O[C@@H](O[C@@H]2OC=C([C@@H](CC(O)=O)[C@H]2C=C)C(O)=O)[C@H](O)[C@@H](O)[C@@H]1O
Lignans		
Acetoxypinoresinol	$C_{22}H_{24}O_8$	COC1=C(O)C=CC(=C1)C1OCC2(OC(C)=O)C1COC2C1=CC(OC)=C(O)C=C1
Berchemol	$C_{20}H_{24}O_7$	COC1=C(C=CC(=C1)CC2COC(C2(CO)O)C3=CC(=C(C=C3)O)OC)O
Hydroxypinoresinol	$C_{20}H_{22}O_7$	COC1=C(O)C=CC(=C1)C1OCC2(O)C1COC2C1=CC(OC)=C(O)C=C1
Olivil	$C_{20}H_{24}O_7$	COC1=C(O)C=CC(C[C@@]2(O)CO[C@@H]([C@H]2CO)C2=CC(OC)=C(O)C=C2)=C1
Syringaresinol	$C_{22}H_{26}O_8$	COC1=CC(=CC(OC)=C1O)C1OCC2C1COC2C1=CC(OC)=C(O)C(OC)=C1
Hydroxy-isochromans		
1-(3′-methoxy-4′-hydroxy)-phenyl-6,7-dihydroxy-isochroman	$C_{16}H_{16}O_5$	COC1=C(O)C=CC(=C1)C1=C(O)C(O)=CC2=C1COCC2
1-phenyl-6,7-dihydroxy-isochroman	$C_{15}H_{14}O_3$	OC1=C(O)C=C2C(OCCC2=C1)C1=CC=CC=C1
Triterpenic acids		
Maslinic acid	$C_{30}H_{48}O_4$	CC1(C)CC[C@@]2(CC[C@]3(C)C(=CC[C@@H]4[C@@]5(C)C[C@@H](O)[C@H](O)C(C)(C)[C@@H]5CC[C@@]34C)[C@@H]2C1)C(O)=O
Oleanolic acid	$C_{30}H_{48}O_3$	CC1(C)CC[C@@]2(CC[C@]3(C)C(=CC[C@@H]4[C@@]5(C)CC[C@H](O)C(C)(C)[C@@H]5CC[C@@]34C)[C@@H]2C1)C(O)=O
Coumarins		

Compound	Molecular Formula	SMILES
Aesculin	$C_{15}H_{15}O_9$	OC[C@H]1O[C@@H](OC2=C(O)C=C3OC(=O)C=CC3=C2)[C@H](O)[C@@H](O)[C@@H]1O
Cichoriin	$C_{15}H_{16}O_9$	C1=CC(=O)OC2=CC(=C(C=C21)O)OC3C(C(C(C(O3)CO)O)O)O
Esculetin	$C_9H_6O_4$	C1=CC(=O)OC2=CC(=C(C=C21)O)O
Scopoletin	$C_{10}H_8O_4$	COC1=C(C=C2C(=C1)C=CC(=O)O2)O
Other compounds		
Abscisic acid	$C_{15}H_{20}O_4$	C\C(\C=C\[C@@]1(O)C(C)=CC(=O)CC1(C)C)=C\C(O)=O
Azelaic acid	$C_9H_{16}O_4$	OC(=O)CCCCCCCC(O)=O
Elenolic acid	$C_{11}H_{14}O_6$	COC(=O)C1=CO[C@@H](C)[C@@H](C=O)[C@@H]1CC(O)=O
Elenolic acid 2-O-glucoside (Oleoside 11-methyl ester)	$C_{17}H_{24}O_{11}$	COC(=O)C1=CO[C@@H](O[C@@H]2O[C@H](CO)[C@@H](O)[C@H](O)[C@H]2O)\C(=C\C)[C@@H]1CC(O)=O
Elenolic acid methyl ester	$C_{12}H_{16}O_6$	COC(=O)C[C@H]1[C@H](C=O)[C@H](C)OC=C1C(=O)OC
Hydroxylated form of elenolic acid	$C_{11}H_{14}O_7$	COC(=O)C1=CO[C@@H](CO)[C@@H](C=O)[C@@H]1CC(O)=O
Licodione	$C_{15}H_{12}O_5$	OC1=CC=C(C=C1)C(=O)CC(=O)C1=CC=C(O)C=C1O
Suspensaside	$C_{29}H_{36}O_{16}$	CC1C(C(C(C(O1)OCC2C(C(C(C(O2)OCC(C3=CC(=C(C=C3)O)O)O)O)O)O)OC(=O)C=CC4=CC(=C(C=C4)O)O)O)O)O

SMILES: simplified molecular-input line-entry system

Table S5. Suspect screening results

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Phenolic acids and derivatives											
4-Hydroxybenzoic acid	$C_7H_6O_3$	137.0244	137.0243	4.00	4.45	71.0139	$C_3H_3O_2$	16	Detected	-	2a
						108.0217	$C_6H_4O_2$				
						123.0088	$C_6H_3O_3$				
4-Hydroxyphenylacetic acid	$C_8H_8O_3$	151.0400	151.0402	3.44	4.00	71.0135	$C_3H_3O_2$	13	Detected	Detected	2a
						81.0341	C_5H_5O				
						95.0499	C_6H_7O				
						108.0215	$C_6H_4O_2$				
						123.0448	$C_7H_7O_2$				
						137.0238	$C_7H_5O_3$				
Vanillic acid	$C_8H_8O_4$	167.0349	167.0344	1.43	-	71.0131	$C_3H_3O_2$	11	Detected	Detected	1
						93.0364	C_6H_5O				
						123.0454	$C_7H_7O_2$				
						137.0257	$C_7H_5O_3$				
						149.0209	$C_8H_5O_3$				
Verbascoside	$C_{29}H_{36}O_{15}$	623.1981	623.1983	5.00	6.91	113.0242	$C_5H_5O_3$	7	Detected	Detected	2a
						133.0292	$C_8H_5O_2$				
						153.0566	$C_8H_9O_3$				
						161.0250	$C_9H_5O_3$				
						179.0351	$C_9H_7O_4$				
						241.0714	$C_{11}H_{13}O_6$				
						275.0569	$C_{14}H_{11}O_6$				
						315.1109	$C_{14}H_{19}O_8$				
						461.1676	$C_{20}H_{29}O_{12}$				
Phenolic alcohols and derivatives											

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Calceolarioside	$C_{23}H_{26}O_{11}$	477.1402	477.1406	5.69	7.64	217.0502	$C_{12}H_9O_4$	8	Detected	Detected	2a
						285.0977	$C_{13}H_{17}O_7$				
Hydroxytyrosol acetate	$C_{10}H_{12}O_4$	195.0660	195.0664	6.65	6.48	59.0139	$C_2H_3O_2$	13	Detected	Detected	2a
						121.0295	$C_7H_5O_2$				
						149.0608	$C_9H_9O_2$				
Hydroxytyrosol glucoside	$C_{14}H_{20}O_8$	315.1085	315.1085	3.88	4.15	71.0132	$C_3H_3O_2$	13	Detected	Detected	2a
						105.0337	C_7H_5O				
						113.0228	$C_5H_5O_3$				
						119.0337	$C_3H_8O_4$				
						123.0447	$C_7H_7O_2$				
						135.0446	$C_8H_7O_2$				
						153.0549	$C_8H_9O_3$				
						179.0578	$C_6H_{11}O_6$				
						240.0601	$C_{11}H_{13}O_6$				
Tyrosol glucoside (Salidroside)	$C_{14}H_{20}O_7$	299.1136	299.1135	3.94	4.92	71.0134	$C_3H_3O_2$	9	Detected	Detected	2a
						113.0222	$C_5H_5O_3$				
						137.0599	$C_8H_9O_2$				
Flavonoids											
Apigenin-7-O-glucoside	$C_{21}H_{20}O_{10}$	431.0983	431.0987	5.92	5.38	67.0188	C_4H_3O	7	Detected	Detected	2a
						111.0086	$C_5H_3O_3$				
						143.0353	$C_6H_7O_4$				
						151.0037	$C_8H_5O_3$				
						269.0444	$C_{15}H_9O_5$				
						300.0276	$C_{15}H_8O_7$				
						311.0555	$C_{17}H_1O_6$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Chrysoeriol (Luteolin 3'-methyl ether)	$C_{16}H_{12}O_6$	299.0561	299.0560	8.24	7.41	83.0138	$C_4H_3O_2$	10	Detected	Detected	2a
						107.0139	$C_6H_3O_2$				
						134.0352	$C_8H_6O_2$				
						151.0024	$C_7H_3O_4$				
						158.0369	$C_{10}H_6O_2$				
						200.0464	$C_{12}H_8O_3$				
						227.0345	$C_{13}H_7O_4$				
						256.0376	$C_{14}H_8O_5$				
						284.0327	$C_{15}H_8O_6$				
Diosmin	$C_{28}H_{32}O_{15}$	607.1668	607.1669	5.70	6.00	89.0242	$C_3H_5O_3$	5	Detected	Detected	2a
						151.0401	$C_8H_7O_3$				
						162.0524	$C_6H_{10}O_5$				
						171.0296	$C_7H_7O_5$				
						216.0404	$C_{12}H_8O_4$				
						233.0664	$C_9H_{13}O_7$				
						256.0374	$C_{14}H_8O_5$				
						275.0768	$C_{11}H_{15}O_8$				
						284.0307	$C_{15}H_8O_6$				
						299.0537	$C_{16}H_{11}O_6$				
						301.0351	$C_{15}H_9O_7$				
						307.1014	$C_{12}H_{19}O_9$				
						343.0448	$C_{17}H_{11}O_8$				
						397.1134	$C_{18}H_{21}O_{10}$				
						444.1261	$C_{19}H_{24}O_{12}$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Fustin	$C_{15}H_{12}O_6$	287.0561	287.0560	6.27	5.77	83.0133	$C_4H_3O_2$	9	Detected	Detected	2a
						107.0137	$C_6H_3O_2$				
						125.0240	$C_6H_5O_3$				
						135.0446	$C_8H_7O_2$				
						151.0031	$C_7H_3O_4$				
						161.0236	$C_9H_5O_3$				
						169.0133	$C_7H_5O_5$				
						177.0181	$C_9H_5O_4$				
						185.0252	$C_{11}H_5O_3$				
						203.0352	$C_{11}H_7O_4$				
						269.0462	$C_{15}H_9O_5$				
Luteolin-7-O-glucoside	$C_{21}H_{20}O_{11}$	447.0932	447.0933	5.41	5.07	59.0135	$C_2H_3O_2$	16	Detected	Detected	2a
						133.0289	$C_8H_5O_2$				
						151.0033	$C_7H_3O_4$				
						169.0137	$C_7H_5O_5$				
						211.0387	$C_{13}H_7O_3$				
						227.0330	$C_{13}H_7O_4$				
						256.0386	$C_{14}H_8O_5$				
						285.0399	$C_{15}H_9O_6$				
						327.0497	$C_{17}H_{11}O_7$				
Luteolin-7,4′-O-diglucoside	$C_{27}H_{30}O_{16}$	609.1461	609.1463	5.45	5.14	113.0233	$C_5H_5O_3$	12	Detected	Detected	2a
						151.0027	$C_7H_3O_4$				
						178.9983	$C_8H_3O_5$				
						255.0297	$C_{14}H_7O_5$				
						271.0252	$C_{14}H_7O_6$				
						300.0282	$C_{15}H_8O_7$				
						343.0469	$C_{17}H_{11}O_8$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
						591.1407	$C_{27}H_{27}O_{15}$				
Naringenin	$C_{15}H_{12}O_5$	271.0611	271.0616	7.41	7.48	119.0504	C_8H_7O	6	Detected	-	2a
						145.0294	$C_9H_5O_2$				
						173.0242	$C_{10}H_5O_3$				
						177.0163	$C_9H_5O_4$				
						187.0369	$C_{11}H_7O_3$				
Quercetin-3-O-rutinoside (Rutin)	$C_{27}H_{30}O_{16}$	609.1461	609.1465	4.61	4.26	113.0233	$C_5H_5O_3$	12	Detected	Detected	2a
						151.0027	$C_7H_3O_4$				
						161.0435	$C_6H_9O_5$				
						272.0300	$C_{14}H_8O_6$				
						300.0282	$C_{15}H_8O_7$				
						343.0469	$C_{17}H_{11}O_8$				
						447.0923	$C_{21}H_{19}O_{11}$				
Taxifolin	$C_{15}H_{12}O_7$	303.0510	303.0517	4.86	-	83.0136	$C_4H_3O_2$	5	Detected	-	1
						123.0445	$C_7H_7O_2$				
						125.0245	$C_6H_5O_3$				
						137.0232	$C_7H_5O_3$				
						151.0047	$C_7H_3O_4$				
						175.0393	$C_{10}H_7O_3$				
						193.0513	$C_{10}H_9O_4$				
						217.0515	$C_{12}H_9O_4$				
						285.0450	$C_{15}H_9O_6$				
Vicenin-2	$C_{27}H_{30}O_{15}$	593.1511	593.1518	4.12	3.92	151.0396	$C_8H_7O_3$	6	Detected	Detected	2a
						325.0698	$C_{18}H_{13}O_6$				
						353.0661	$C_{19}H_{13}O_7$				
						383.0755	$C_{20}H_{15}O_8$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
						413.0889	$C_{21}H_{17}O_9$				
						473.1113	$C_{23}H_{21}O_{11}$				
						503.1198	$C_{24}H_{23}O_{12}$				
						575.1431	$C_{27}H_{27}O_{14}$				
					Secoiridoids						
Decarboxymethyl ligstroside aglycone (Oleocanthal)	$C_{17}H_{20}O_5$	303.1237	303.1239	6.47	6.76	69.0343	C_4H_5O	4	-	Detected	2a
						95.0498	C_6H_7O				
						113.0235	$C_5H_5O_3$				
						121.0294	$C_7H_5O_2$				
						123.0448	$C_7H_7O_2$				
						137.0598	$C_8H_9O_2$				
						165.0553	$C_9H_9O_3$				
						183.0661	$C_9H_{11}O_4$				
						233.0819	$C_{13}H_{13}O_4$				
Decarboxymethyl oleuropein aglycone (Oleacein)	$C_{17}H_{20}O_6$	319.1185	319.1188	5.69	6.14	69.0346	C_4H_5O	11	Detected	Detected	2a
						95.0499	C_6H_7O				
						113.0227	$C_5H_5O_3$				
						123.0448	$C_7H_7O_2$				
						139.0390	$C_7H_7O_3$				
						139.0757	$C_8H_{11}O_2$				
						165.0541	$C_9H_9O_3$				
						183.0658	$C_9H_{11}O_4$				
Demethyl oleuropein	$C_{24}H_{30}O_{13}$	525.1613	525.1616	4.21	4.31	163.0374	$C_9H_7O_3$	14	Detected	Detected	2b
						389.1023	$C_{16}H_{21}O_{11}$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Fraxamoside	$C_{25}H_{30}O_{13}$	537.1613	537.1616	4.35	5.16	133.0293 161.0238 165.0547 179.0335 205.0501 221.0472 235.0597 323.0777	$C_8H_5O_2$ $C_9H_5O_3$ $C_9H_9O_3$ $C_9H_7O_4$ $C_{11}H_9O_4$ $C_{11}H_9O_5$ $C_{12}H_{11}O_5$ $C_{15}H_{15}O_8$	9	Detected	Detected	2a
10-Hydroxy-10-Methyl oleuropein aglycone	$C_{20}H_{24}O_9$	407.1347	407.1350	6.60	6.75	111.0087 121.0295 179.0351 241.0871	$C_5H_3O_3$ $C_7H_5O_2$ $C_9H_7O_4$ $C_{15}H_{13}O_3$	10	Detected	Detected	2b
10-Hydroxy decarboxymethyl oleuropein aglycone	$C_{17}H_{20}O_7$	335.1136	335.1136	4.58	5.52	85.0296 121.0292 153.0557 199.0613	$C_4H_5O_2$ $C_7H_5O_2$ $C_8H_9O_3$ $C_9H_{11}O_5$	11	Detected	Detected	2b
10-Hydroxy oleuropein aglycone	$C_{19}H_{22}O_9$	393.1193	393.1195	4.63	5.48	137.0244 181.0502	$C_7H_5O_3$ $C_9H_9O_4$	12	Detected	Detected	2b
Ligstroside	$C_{25}H_{32}O_{12}$	523.1821	523.1820	6.74	6.80	69.0340 89.0242 101.0240 127.0400 139.0032 165.0571 171.0293	C_4H_5O $C_3H_5O_3$ $C_4H_5O_3$ $C_6H_7O_3$ $C_6H_3O_4$ $C_9H_9O_3$ $C_7H_7O_5$	11	Detected	Detected	2a

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
						223.0629	$C_{11}H_{11}O_5$				
						259.0966	$C_{15}H_{15}O_4$				
						291.0881	$C_{15}H_{15}O_6$				
						361.1305	$C_{19}H_{21}O_7$				
Ligstroside aglycone	$C_{19}H_{22}O_7$	361.1291	361.1293	6.79	6.83	69.0346	C_4H_5O	21	Detected	Detected	2a
						111.0077	$C_5H_2O_3$				
						137.0608	$C_8H_9O_2$				
						195.0663	$C_{10}H_{11}O_4$				
						259.0975	$C_{15}H_{15}O_4$				
						291.0875	$C_{15}H_{15}O_6$				
Nuzhenide	$C_{31}H_{42}O_{17}$	685.2349	685.2346	6.20	6.19	89.0241	$C_3H_5O_3$	12	-	Detected	2a
						135.0453	$C_8H_7O_2$				
						223.0612	$C_{11}H_{11}O_5$				
						291.0871	$C_{15}H_{15}O_6$				
						369.0825	$C_{16}H_{17}O_{10}$				
						453.1401	$C_{21}H_{25}O_{11}$				
						563.1616	$C_{23}H_{31}O_{16}$				
Oleoside	$C_{16}H_{22}O_{11}$	389.1089	389.1090	6.79	*	139.0032	$C_6H_3O_4$	4	Detected	Detected	2a
						165.0552	$C_9H_9O_3$				
						183.0664	$C_9H_{11}O_4$				
Oleuropein aglycone	$C_{19}H_{22}O_8$	377.1241	377.1243	7.39	6.88	95.0496	C_6H_7O	19	Detected	Detected	2a
						111.0087	$C_5H_3O_3$				
						139.0389	$C_7H_7O_3$				
						171.0286	$C_7H_7O_5$				
						191.0346	$C_{10}H_7O_4$				
						275.0556	$C_{14}H_{11}O_6$				

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Secologanoside	$C_{16}H_{22}O_{11}$	389.1089	389.1088	1.28	2.79	95.0499	C_6H_7O	4	Detected	Detected	2a
						101.0244	$C_4H_5O_3$				
						139.0752	$C_8H_{11}O_2$				
						165.0550	$C_9H_9O_3$				
						183.0645	$C_9H_9O_4$				
						345.1100	$C_{15}H_{21}O_9$				
Triterpenic acids											
Maslinic acid	$C_{30}H_{48}O_4$	471.3484	471.3481	12.86	12.58	393.3163	$C_{28}H_{41}O$	15	Detected	Detected	2a
						405.3158	$C_{29}H_{41}O$				
						423.3256	$C_{29}H_{43}O_2$				
						437.3061	$C_{29}H_{41}O_3$				
Oleanolic acid	$C_{30}H_{48}O_3$	455.3535	455.3536	13.91	12.69**	120.0940	C_9H_{12}	16	Detected	Detected	2a
						152.1202	$C_{10}H_{16}O$				
						407.3313	$C_{29}H_{43}O$				
						441.3430	$C_{29}H_{45}O_3$				
Coumarins											
Aesculin	$C_{15}H_{15}O_9$	338.0643	338.0645	5.41	4.01	112.0164	$C_5H_4O_3$	16	Detected	-	2a
						153.0189	$C_7H_5O_4$				
						161.0248	$C_9H_5O_3$				
						171.0287	$C_7H_7O_5$				
						220.0581	$C_8H_{12}O_7$				
						268.0577	$C_{12}H_{12}O_7$				
						311.0761	$C_{14}H_{15}O_8$				
Other compounds											

Compound	Molecular Formula	[M-H]⁻ m/z calc.	[M-H]⁻ m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Elenolic acid	$C_{11}H_{14}O_6$	241.0714	241.0716	4.09	4.26	95.0494 121.0289 127.0396 139.0029 139.0410 149.0236 165.0572	C_6H_7O $C_7H_5O_2$ $C_6H_7O_3$ $C_6H_3O_4$ $C_7H_7O_3$ $C_8H_5O_3$ $C_9H_9O_3$	24	Detected	Detected	2a
Elenolic acid 2-O-glucoside (Oleoside 11-methyl ester)	$C_{17}H_{24}O_{11}$	403.1245	403.1242	2.96	2.12	113.0248 119.0352 181.0512 310.1163 371.0900	$C_5H_5O_3$ $C_4H_8O_4$ $C_9H_9O_4$ $C_{15}H_{18}O_7$ $C_{16}H_{19}O_{10}$	11	Detected	Detected	2a
Hydroxylated form of elenolic acid	$C_{11}H_{14}O_7$	257.0667	257.0671	2.92	*	137.0603 181.0535	$C_8H_9O_2$ $C_9H_9O_4$	4	Detected	-	3
Licodione	$C_{15}H_{12}O_5$	271.0611	271.0616	7.19	7.63	83.0154 119.0506 151.0037 177.0160 187.0364	$C_4H_3O_2$ C_8H_7O $C_7H_3O_4$ $C_9H_5O_4$ $C_{11}H_7O_3$	5	Detected	-	2a

Compound	Molecular Formula	[M-H]- m/z calc.	[M-H]- m/z exp.	t_R exp. (min)	t_R QSRR (min)	Fragments m/z	Elemental Formula	Peak score A/I	Leaf	Drupe	Level Ident.
Suspensaside	$C_{29}H_{36}O_{16}$	639.1930	639.1934	4.46	6.01	113.0244	$C_5H_5O_3$	7	-	Detected	2a
						127.0399	$C_6H_7O_3$				
						135.0442	$C_8H_7O_2$				
						161.0233	$C_9H_5O_3$				
						179.0335	$C_9H_7O_4$				
						241.0694	$C_{11}H_{13}O_6$				
						265.0743	$C_{13}H_{13}O_6$				
						325.0944	$C_{15}H_{17}O_8$				
						459.1525	$C_{20}H_{27}O_{12}$				
						479.1560	$C_{23}H_{27}O_{11}$				
						621.1832	$C_{29}H_{33}O_{15}$				

Peak Score (A/I): ratio of peak area to intensity

Level Ident.: Level of identification (Level 1 corresponds to confirmed structures with a reference standard; level 2a: evidence by spectra matching from literature or library and level 2b: diagnostic evidence where no other structure fits the experimental MS/MS information; level 3 for tentative candidate).

t_R QSRR: Predicted retention time with the in-house QSRR model [1,2]

*t_R: The retention time prediction results are not reliable and other verification methods such as MS/MS fragmentation pattern should be applied.

**t_R: The retention time prediction result is not reliable because the compound is found to be outside of applicability domain of the model [3,4].

Table S6. Percentages of increase or decrease of the analytical signals during the experimental time periods 3 to 6 min and 6 to 10 min

Compounds	% increase in analytical signal (3-6 min infusion)	% increase in analytical signal (6-10 min infusion)
Target compounds		
Gallic acid	99	98
Tyrosol	129	231
Vanillin	119	113
Luteolin	85	72
Suspect compounds		
4-Hydroxybenzoic acid	99	101
4-Hydroxyphenylacetic acid	128	119
Vanillic acid	104	107
Verbascoside	129	125
Calceolarioside	76	80
Hydroxytyrosol glucoside	125	118
Tyrosol glucoside (Salidroside)	118	117
Apigenin-7-O-glucoside	125	379
Diosmin	64	71
Luteolin-7-O-glucoside	94	103
Luteolin-7,4′-O-diglucoside	128	136
Quercetin-3-O-rutinoside (Rutin)	120	124
Vicenin-2	120	112
Demethyl oleuropein	229	127
Fraxamoside	110	104
10-Hydroxy-10-Methyl oleuropein aglycone	105	103
10-Hydroxy decarboxymethyl oleuropein aglycone	91	249
Ligstroside	128	115
Ligstroside aglycone	127	111
Oleoside	114	115
Oleuropein aglycone	122	123
Secologanoside	114	122
Elenolic acid 2-O-glucoside (Oleoside 11-methyl ester)	122	117

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