SUPPORTING INFORMATION

Application of LC-ion mobility spectrometry-MS-based metabolomics to investigate the basal chemical profile of olive cultivars differing in *Verticillum dahliae* resistance

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Table S1. $^{TIMS}CCS_{N2}$ Database of many compounds detected in olive-derived matrices by LC-ESI-TimsTOF MS/MS profiling along with its presence in the olive root, stem and leaf organ.

			For experimental $[M-H]^-$					Detected in:		
Proposed compound	**Molecular Formula**	**Rt (min)**	***m/z exp***	**Error (ppm)**	**mSigma**	**$^{TIMS}CCS_{N2}$ (Å²)♦**	**Main fragments via MS/MS**	**Root**	**Stem**	**Leaf**
Organic acids										
*quinic acid**	$C_7H_{12}O_6$	1.24	191.0562	0.52	4.4	134.3	127.0416; 93.0344; 85.0294	x	x	x
citric acid	$C_6H_8O_7$	1.26	191.0197	-0.01	11.9	126.5	111.0092; 87.0087; 85.0291	x	x	x
Iridoids										
loganic acid	$C_{16}H_{24}O_{10}$	1.30	375.1296	0.07	22.7	184.7	213.0764; 169.0876; 151.0752; 125.0606; 113.0244; 107.0499	x	x	x
7-deoxyloganic acid	$C_{16}H_{24}O_9$	4.82	359.1347	-0.36	6.1	182.4	197.0814; 153.0923; 135.0817	x	x	-
11-hydroxyiridodial glucoside pentaacetate	$C_{26}H_{36}O_{13}$	5.66	555.2082	-0.06	9.9	222.3	225.1134; 183.0659; 167.0717; 151.0406	x	x	-
Coumarins										
aesculin	$C_{15}H_{16}O_9$	4.44	339.0721	-0.06	27.0	174.6	177.0192; 133.0299	x	x	-
aesculetin	$C_9H_6O_4$	6.39	177.0194	0.39	10.6	127.5	149.0244; 133.0300; 105.0345; 89.0401	x	x	x
Simple phenols and derivatives										
hydroxytyrosol glucoside (is. 1, main peak)	$C_{14}H_{20}O_8$	4.33	315.1084	-0.31	6.4	163.1	153.0559; 135.0451; 123.0459	x	x	x
hydroxytyrosol glucoside (is.2)			315.1085	0.04	2.8	171.8	153.0556; 135.0450; 123.0453	x	x	x
*hydroxytyrosol**	$C_8H_{10}O_3$	4.49	153.0557	-0.38	5.6	128.8	123.0455; 109.0293	-	x	x
tyrosol glucoside	$C_{14}H_{20}O_7$	4.69	299.1136	-0.17	10.0	161.4	137.0622; 119.0425	x	x	x
*tyrosol**	$C_8H_{10}O_2$	5.00	137.0611	1.86	3.5	127.6	119.0449; 107.0508	-	-	-
*verbascoside**	$C_{29}H_{36}O_{15}$	5.73	623.1979	-0.25	8.2	223.2	461.1663; 179.0351; 161.0242; 135.0446	x	x	x
phenylethyl primeveroside	$C_{19}H_{28}O_{10}$	5.78	415.1609	-0.12	4.6	202.2	149.0444	x	x	x
isoverbascoside	$C_{29}H_{36}O_{15}$	6.17	623.1981	0.08	5.5	223.4	461.1665; 161.0245	x	-	-
Lignans and derivatives										
cycloolivil glucoside (is.1, main peak)	$C_{26}H_{34}O_{12}$	5.03	537.1977	-0.09	3.8	231.4	375.1450; 195.0661; 179.0710	x	x	-
cycloolivil glucoside (is.2, main peak)			537.1976	-0.32	2.1	208.9	375.1446; 345.1372; 195.0661; 179.0716	x	x	-
cycloolivil glucoside (is.3)	$C_{26}H_{34}O_{12}$	5.16	537.1975	-0.27	21.0	214.5	375.1449; 195.0665; 179.0700	x	x	-
olivil	$C_{20}H_{24}O_7$	5.54	375.1449	-0.17	11.0	197.8	360.1227; 345.1360; 327.1252; 195.0670; 179.0713	x	x	-
cycloolivil			375.1448	-0.33	10.2	205.6	360.1228; 345.1358	x	x	-
(+)-1-acetoxypinoresinol 4'-ß-D-glucoside (is.1, main peak)	$C_{28}H_{34}O_{13}$	6.09	577.1928	0.23	8.4	210.7	415.1395	x	x	-
8-acetoxypinoresinol 4-glucoside (is.2)			577.1927	0.02	3.8	227.9	415.1404	x	x	-
hydroxypinoresinol glucoside (is.1)	$C_{26}H_{32}O_{12}$	6.33	535.1820	-0.16	2.8	215.9	373.1289; 355.1189; 295.0998	x	x	-
hydroxypinoresinol glucoside (is.2, main peak)			535.1822	0.25	8.9	229.5	373.1290	x	x	-
1-acetoxypinoresinol	$C_{22}H_{24}O_8$	7.15	415.1398	-0.02	12.0	203.5	325.1066; 280.0728; 181.0508; 151.0399; 136.0163	x	x	-
Secoiridoids and derivatives										
aldehydic form of decarboxymethyl elenolic acid glucoside (is.1)	$C_{16}H_{26}O_{10}$	1.27	377.1452	-0.15	8.6	188.8	197.0821; 153.0921	x	x	x
oleoside / secologanoside	$C_{16}H_{22}O_{11}$	1.29	389.1090	0.08	8.9	184.6	345.1164; 209.0446; 183.0663; 165.0519; 121.0663; 113.0250	x	x	x
oleoside / secologanoside	$C_{16}H_{22}O_{11}$	1.32	389.1088	-0.44	11.7	189.5	345.1161; 227.0558; 209.0445; 183.0669; 121.0665; 113.0253	x	x	x
elenolic acid glucoside (is.1)	$C_{17}H_{24}O_{11}$	2.14	403.1245	-0.36	15.7	192.5	371.0975; 223.0598; 181.0504; 179.0557; 127.0393; 101.0243	x	x	x
elenolic acid glucoside (is.2)	$C_{17}H_{24}O_{11}$	2.69	403.1246	-0.02	10.4	189.9	371.0978; 223.0607; 179.0561; 127.0419; 101.0238	x	x	x
aldehydic form of decarboxymethyl elenolic acid glucoside (is.2)	$C_{16}H_{26}O_{10}$	4.23	377.1452	0.02	8.8	188.6	197.0823; 153.0915	x	x	x
elenolic acid glucoside (is.3)	$C_{17}H_{24}O_{11}$	4.49	403.1245	-0.01	13.4	192.1	371.0975; 223.0601; 181.0493; 165.0555; 121.0296; 101.0241	x	x	x
elenolic acid dihexose derivate	$C_{25}H_{38}O_{18}$	4.85	625.1986	0.05	6.9	231.5	223.0601; 179.0564; 119.0353	x	x	x
demethyl oleuropein	$C_{24}H_{30}O_{13}$	4.95	525.1606	0.01	8.9	213.5	481.1694; 389.1085; 209.0442; 195.0663; 121.0670	x	x	x
elenolic acid dihexose	$C_{23}H_{34}O_{15}$	5.16	565.1775	-0.20	5.9	234.9	403.1239; 371.0981; 223.0603; 113.0224; 101.0232; 89.0232	x	x	x
demethyl ligstroside	$C_{24}H_{30}O_{12}$	5.23	509.1663	-0.22	27.1	208.8	347.1128; 277.0713; 233.0801; 165.0554; 121.0680	x	x	x
hydroxy oleuropein (is.1, main peak)	$C_{25}H_{32}O_{14}$	5.60	555.1719	0.03	15.3	218.9	537.1597; 403.1242; 393.1190; 323.0770; 151.0386	x	x	x
hydroxy oleuropein (is.2)			555.1721	-0.03	13.2	227.6	537.1595; 403.1241; 151.0383	x	x	x
neonuzhenide / oleuropein glucoside (is.1)	$C_{31}H_{42}O_{18}$	5.63	701.2293	-0.72	19.1	245.5	539.1770; 377.1241; 307.0795; 275.0925	x	x	-
elenolic acid glucoside (is.4)	$C_{17}H_{24}O_{11}$	5.94	403.1246	0.00	8.6	190.1	223.0603; 121.0289; 113.0228; 101.0246	x	x	x

Secoiridoids and derivatives										
nuzhenide	$C_{31}H_{42}O_{17}$	6.03	685.2347	-0.34	19.0	241.1	523.1813; 453.1391; 421.1499; 299.1132	x	x	x
neonuzhenide / oleuropein glucoside (is.2)	$C_{31}H_{42}O_{18}$	6.10	701.2297	-0.22	16.1	241.8	539.1773; 377.1238; 307.0830; 275.0925	x	x	-
methoxyoleuropein	$C_{26}H_{34}O_{14}$	6.52	569.1867	-0.55	28.2	223.2	537.1587; 403.1235; 223.0604; 165.0570; 121.0292	x	x	x
neonuzhenide / oleuropein glucoside (is.3)	$C_{31}H_{42}O_{18}$	6.54	701.2296	-0.33	19.2	248.9	539.1769; 377.1236; 307.0816; 275.0928	-	x	x
*oleuropein**	$C_{25}H_{32}O_{13}$	6.66	539.1718	0.19	4.5	217.5	403.1233; 377.1234; 307.0822; 275.0924; 223.0609; 179.0558	x	x	x
elenolic acid glucoside (is.5)	$C_{17}H_{24}O_{11}$	6.86	403.1246	-0.04	6.9	190.4	371.0967; 223.0604; 181.0483; 127.0409; 101.0249; 89.0193	x	x	x
lucidumoside C	$C_{27}H_{36}O_{14}$	7.13	583.2032	0.03	14.8	229.1	403.1224; 223.0593; 179.0541; 151.0399	x	x	x
ligstroside	$C_{25}H_{32}O_{12}$	7.26	523.1824	0.37	9.0	214.7	361.1290; 291.0879; 259.0976; 223.0621; 101.0245	x	x	x
oleuroside	$C_{25}H_{32}O_{13}$	7.35	539.1766	-0.70	10.9	217.1	403.1230; 377.1244; 345.0990; 307.0824; 275.0926; 223.0610	-	x	x
oleuropein aglycone (is.1)	$C_{19}H_{22}O_8$	8.03	377.1239	-0.73	3.2	186.0	307.0820; 275.0572; 149.0241; 139.0389; 111.0082; 95.0500	x	x	x
oleuropein aglycone (is.2)	$C_{19}H_{22}O_8$	8.33	377.1243	0.41	2.3	185.2	307.0822; 275.0564; 149.0234; 139.0390; 127.0408; 111.0088	x	x	x
oleuropein aglycone (is.3)	$C_{19}H_{22}O_8$	9.00	377.1242	-0.02	17.9	184.8	275.0564; 149.0237; 139.0399; 127.0407; 121.0315	x	x	x
Flavonoids										
dihydroquercetin-O-glucoside (is.1)	$C_{21}H_{22}O_{12}$	4.67	465.1036	-0.54	12.9	191.8	303.0505; 285.0399; 177.0191; 125.0261	-	x	-
*catechin**	$C_{15}H_{14}O_6$	4.80	289.0721	1.23	3.3	156.8	245.0810; 203.0744; 179.0362	-	-	-
*catechin**			289.0722	1.51	1.2	169.5	245.0811; 203.0746; 179.0358	-	-	-
dihydrokaempferol-O-glucoside	$C_{21}H_{22}O_{11}$	4.91	449.1089	0.37	10.6	186.3	287.0550; 259.0633; 243.0664; 151.0034; 125.0245	-	x	-
dihydroquercetin-O-glucoside (is.2)	$C_{21}H_{22}O_{12}$	5.40	465.1036	0.42	15.7	192.5	303.0504; 285.0406	-	x	-
taxifolin (dihydroquercetin)	$C_{15}H_{12}O_7$	5.77	303.0510	-0.07	3.8	164.7	285.0409; 177.0199; 125.0263	-	x	-
naringenin-O-glucoside	$C_{21}H_{22}O_{10}$	6.26	433.1138	-0.02	11.2	183.1	271.0615; 151.0018; 119.0515	-	x	x
dihydrokaempferol	$C_{15}H_{12}O_6$	6.30	287.0560	-0.30	2.9	163.4	259.0598; 243.0661; 177.0561; 151.0039; 125.0244	-	x	-
*rutin**	$C_{27}H_{30}O_{16}$	6.36	609.1471	1.63	2.9	232.4	301.0349; 300.0252	-	x	x
*luteolin-O-glucoside (is.1) (luteolin-7-O-glucoside)**	$C_{21}H_{20}O_{11}$	6.46	447.0934	-0.06	19.6	210.2	285.0408	-	x	x
quercetin-O-glucoside (is.1)	$C_{21}H_{20}O_{12}$	6.50	463.0879	-0.48	17.1	202.1	301.0347; 300.0251	-	x	x
apigenin-O-rutinoside (is.1)	$C_{27}H_{30}O_{14}$	6.55	577.1563	0.03	10.4	232.7	269.0458	-	-	x
apigenin 7-O-rutinoside (is.2)	$C_{27}H_{30}O_{14}$	6.65	577.1561	0.25	12.0	224.5	269.0458	-	-	x
apigenin-7-O-glucoside	$C_{21}H_{20}O_{10}$	6.73	431.0984	-0.03	10.5	208.1	269.0459	-	x	x
diosmin	$C_{28}H_{32}O_{15}$	6.74	607.1664	-0.75	24.8	231.8	299.0562; 284.0319	-	-	x
chrysoeriol-7-O-glucoside	$C_{22}H_{22}O_{11}$	6.80	461.1089	-0.25	3.7	215.9	446.0858; 299.0561	-	-	x
luteolin-O-glucoside (is.2)	$C_{21}H_{20}O_{11}$	6.85	447.0931	-0.45	8.3	208.4	285.0405; 133.0297	-	x	x
quercetin-O-glucoside (is.2)	$C_{21}H_{20}O_{12}$	6.90	463.0879	-0.71	14.7	210.9	301.0345	-	x	x
luteolin-O-glucoside (is.3)	$C_{21}H_{20}O_{11}$	7.17	447.0933	-0.02	15.4	210.2	285.0405; 284.0331	-	x	x
naringenin	$C_{15}H_{12}O_5$	7.77	271.0613	0.35	1.6	163.0	151.0028; 119.0500	x	x	x
*luteolin**	$C_{15}H_{10}O_6$	8.71	285.0407	0.89	19.3	160.6	217.0516; 199.0409; 175.0401; 151.0038; 133.0291; 107.0139	x	x	x
*apigenin**	$C_{15}H_{10}O_5$	8.80	269.0456	0.04	6.5	157.6	225.0554; 201.0547; 149.0238	x	x	x
Pentacyclic triterpenes										
*maslinic acid**	$C_{30}H_{48}O_4$	13.13	471.3479	-0.30	12.7	223.4	-	x	x	x
betulinic acid	$C_{30}H_{48}O_3$	14.00	455.3531	-0.02	2.6	220.1	-	x	x	x
*oleanolic acid**	$C_{30}H_{48}O_3$	14.14	455.3530	0.32	5.1	220.7	-	x	x	x

*Corroborated with a pure standard

♦The variability in the determination of CCS values, expressed as the coefficient of variation (%CV) across all samples in which each compound was detected, was consistently below 0.148%.

Principal Component Analysis

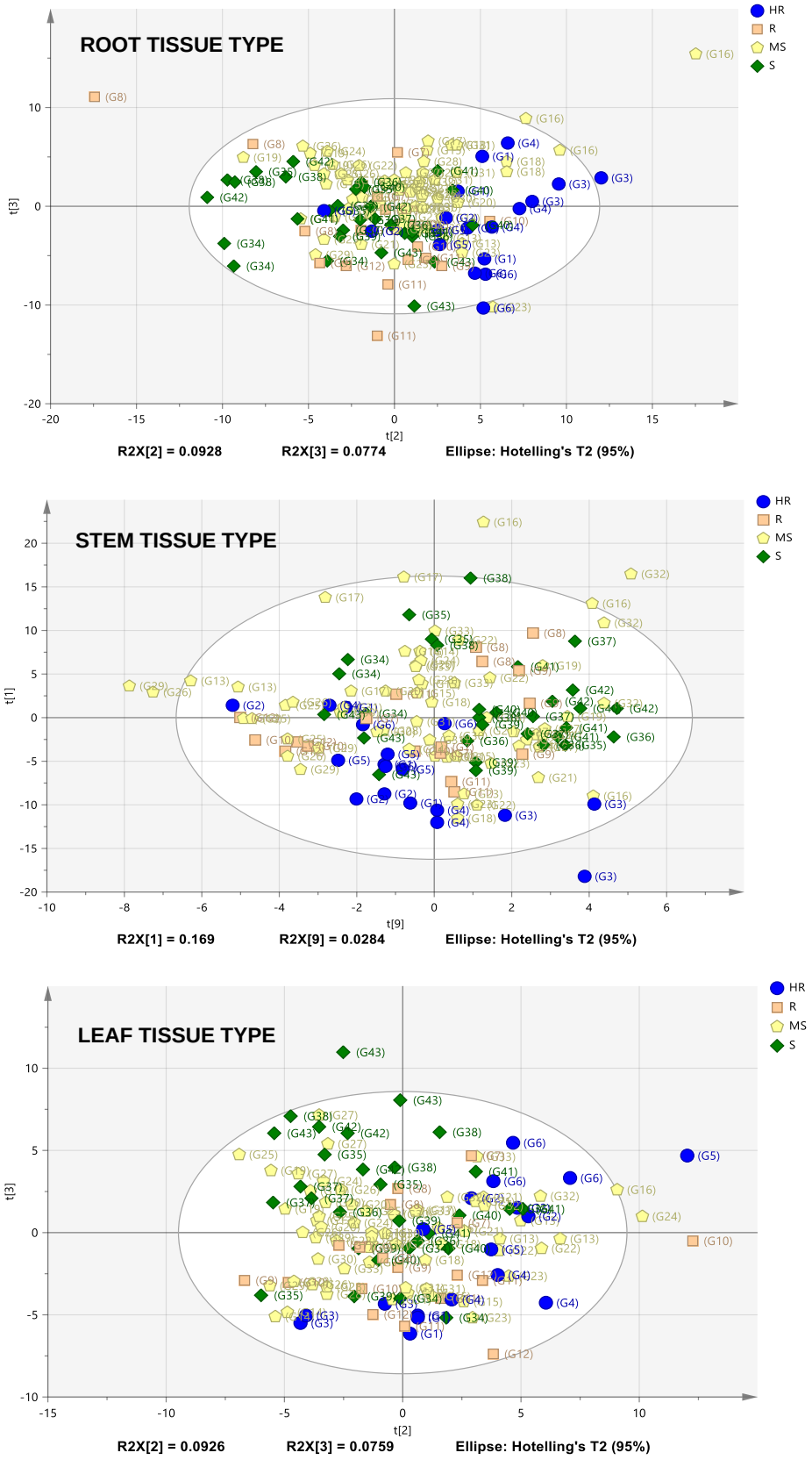
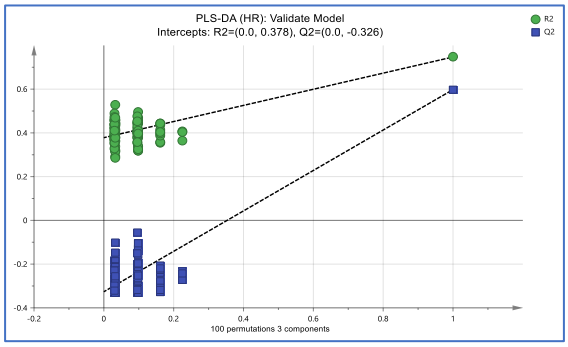


Figure S1. PCA score plots generated in two dimensions (2D) for olive roots, stems, and leaves, using the two most optimal principal components (2PCs) to effectively distinguish between HR and S samples.

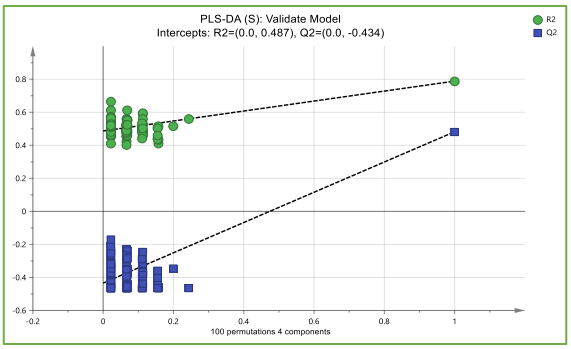
ROOT TISSUE TYPE

	PLS-DA model	A	N	R^2X (cum)	R^2Y (cum)	Q^2 (cum)
(1)-	HR *vs.* Others	3	129	0.283	0.747	0.598
(2)-	S *vs.* Others	4	129	0.318	0.789	0.482

(1)- Permutations PLS-DA **(HR)**



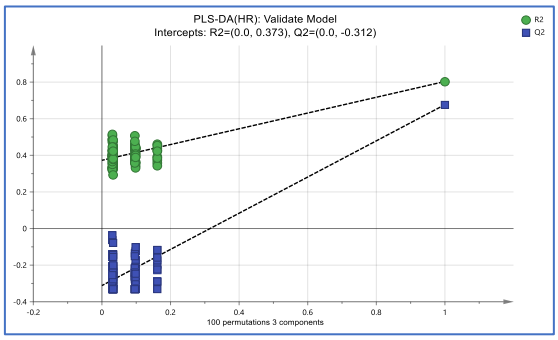
(2)- Permutations PLS-DA **(S)**



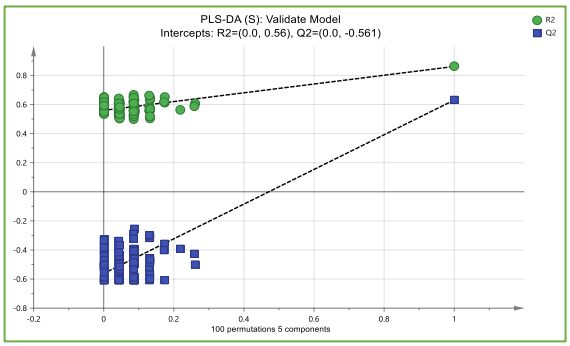
STEM TISSUE TYPE

	PLS-DA model	A	N	R^2X (cum)	R^2Y (cum)	Q^2 (cum)
(1)-	HR *vs.* Others	3	129	0.275	0.803	0.677
(2)-	S *vs.* Others	5	129	0.391	0.861	0.630

(1)- Permutations PLS-DA **(HR)**



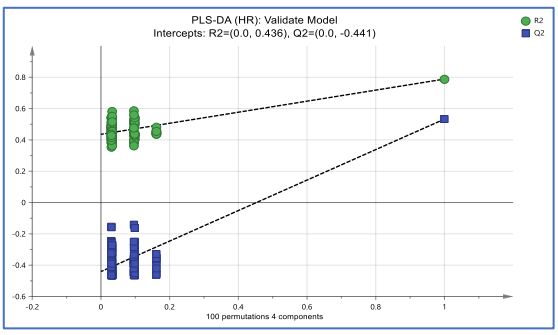
(2)- Permutations PLS-DA **(S)**



LEAF TISSUE TYPE

	PLS-DA model	A	N	R^2X (cum)	R^2Y (cum)	Q^2 (cum)
(1)-	HR *vs.* Others	4	129	0.339	0.788	0.533
(2)-	S *vs.* Others	3	129	0.279	0.666	0.318

(1)- Permutations PLS-DA **(HR)**



(2)- Permutations PLS-DA **(S)**

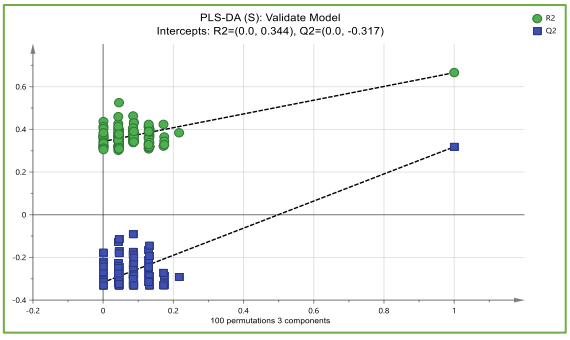


Figure S2. Model quality descriptors (R^2X, R^2Y and Q^2) and permutation tests of PLS-DA models built for each tissue type.

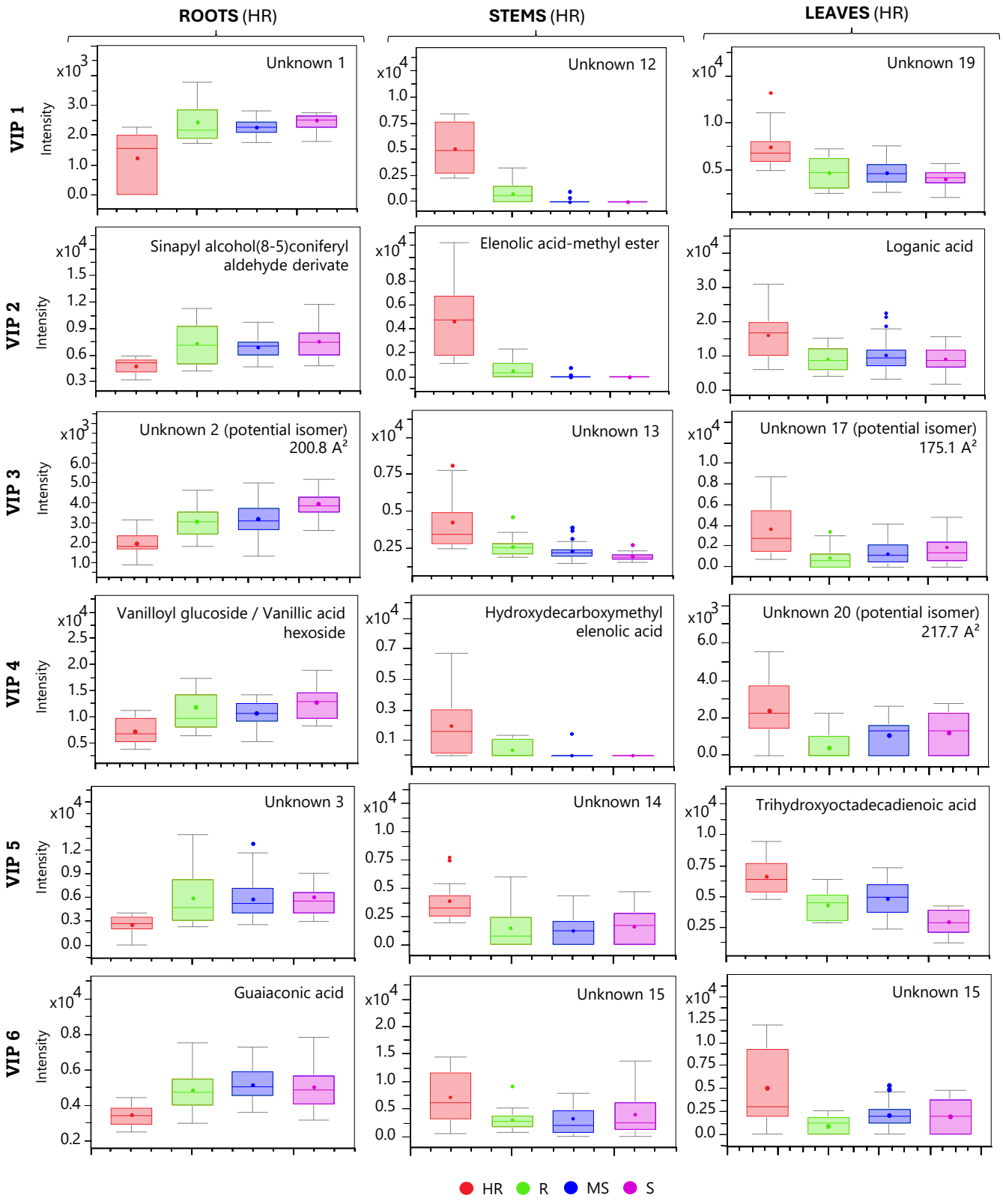


Figure S3. Box and whisker plots of compounds with the highest VIP values from PLS-DA models (HR *vs*. rest and S *vs*. rest) for each olive organ. The representation of unknown compounds that could be potential isomers include the CCS value to avoid any possible misinterpretation.

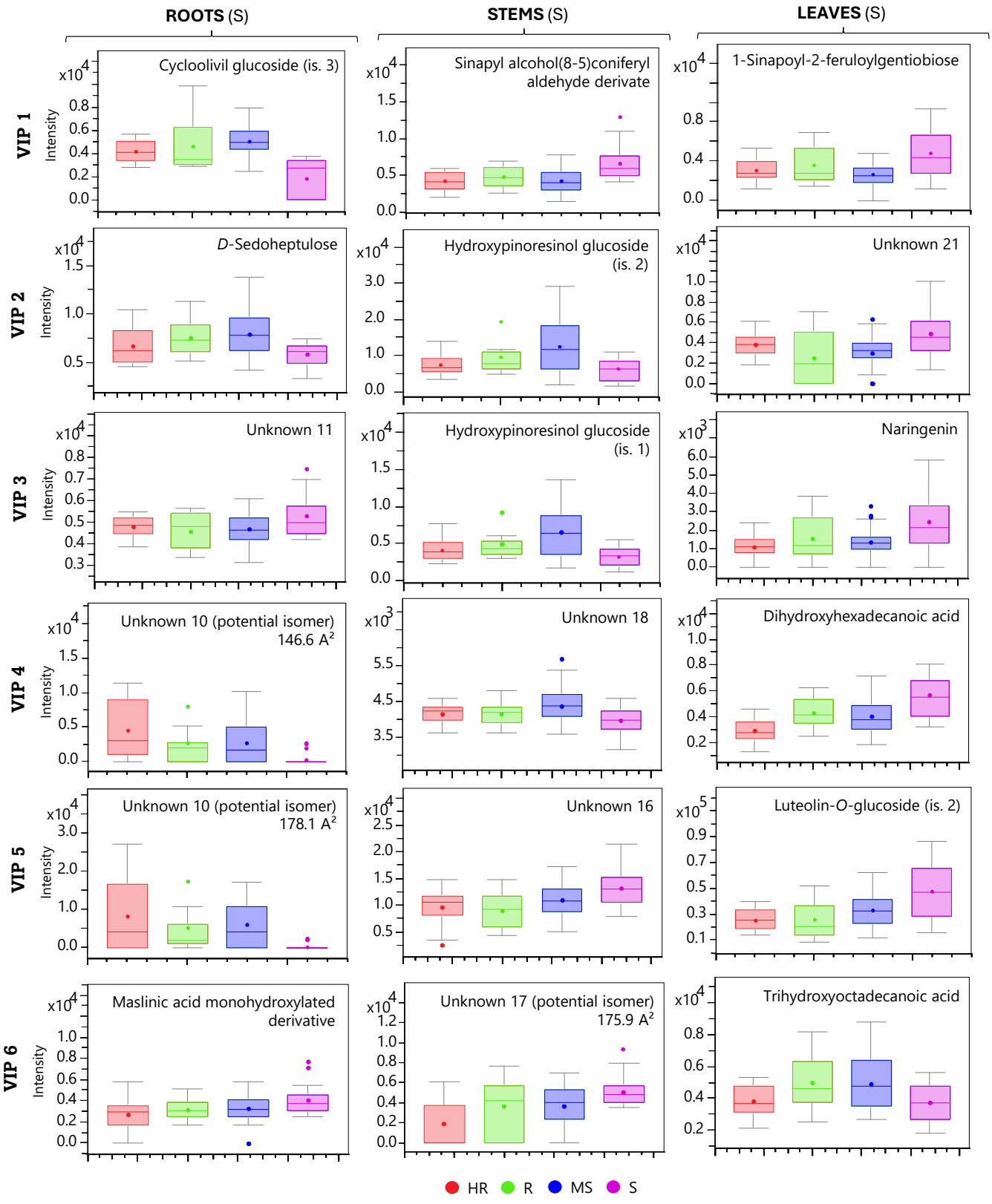


Figure S3 (cont.). Box and whisker plots of compounds with the highest VIP values from PLS-DA models (HR *vs*. rest and S *vs*. rest) for each olive organ. The representation of unknown compounds that could be potential isomers include the CCS value to avoid any possible misinterpretation.

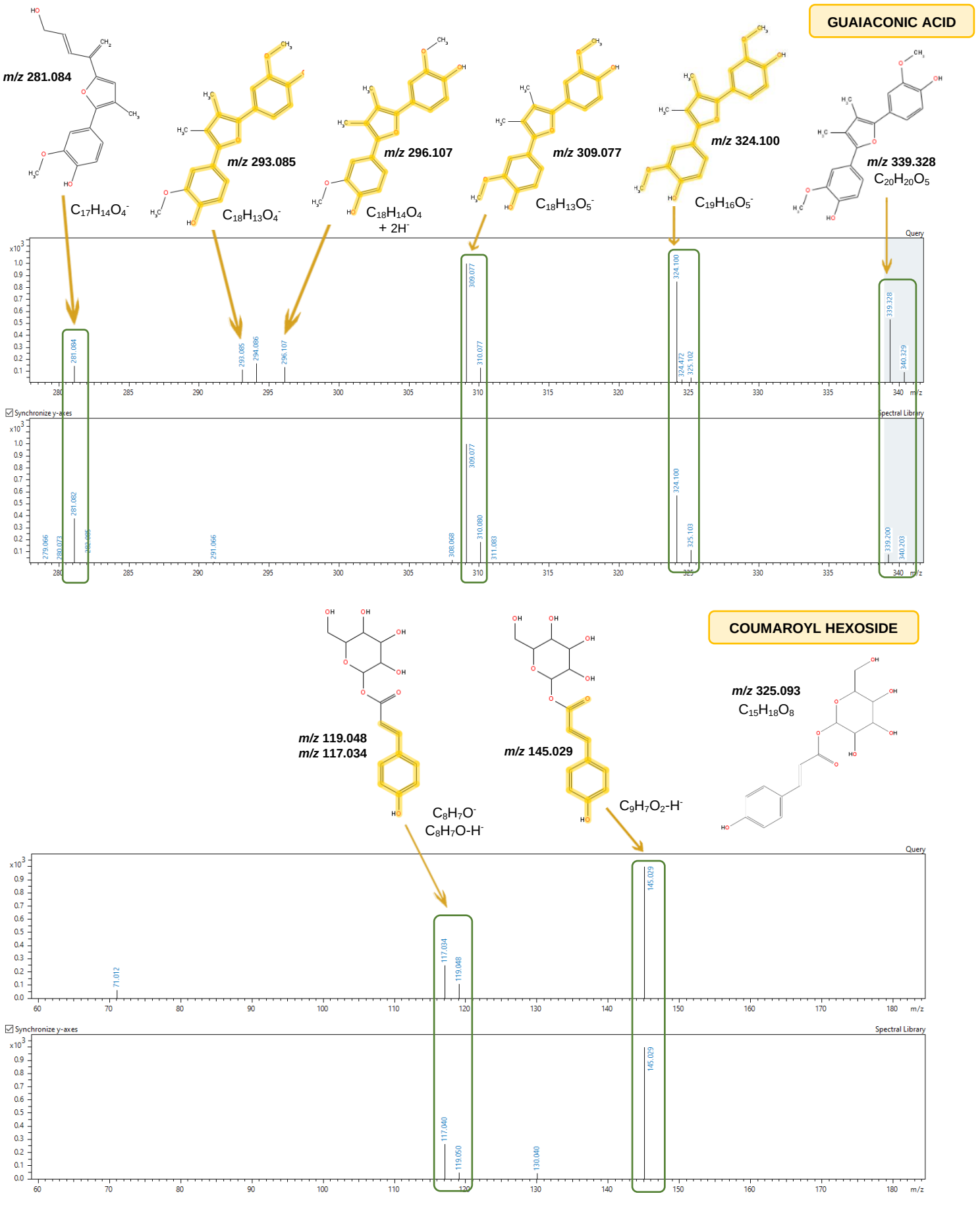


Figure S4. Molecular structure and MetFrag outcomes for guaiaconic and coumaroyl hexoside fragment assignments.