

Table S1: Information about olive variety, region and sub-region of production, harvesting year for all the samples collected and analyzed.

	Sample Coding	Variety	Region	Sub-region	Harvesting Year
1	KOL_LES_50	Kolovi	Lesvos	Lesvos	2020
2	KOL_LES_51	Kolovi	Lesvos	Lesvos	2020
3	KOL_LES_52	Kolovi	Lesvos	Lesvos	2020
4	KOL_LES_53	Kolovi	Lesvos	Lesvos	2020
5	KOL_LES_54	Kolovi	Lesvos	Lesvos	2020
6	KOL_LES_55	Kolovi	Lesvos	Lesvos	2020
7	KOR_ACH_01	Koroneiki	Peloponnese	Achaia	2020
8	KOR_ACH_02	Koroneiki	Peloponnese	Achaia	2020
9	KOR_ACH_03	Koroneiki	Peloponnese	Achaia	2020
10	KOR_ACH_04	Koroneiki	Peloponnese	Achaia	2020
11	KOR_ACH_05	Koroneiki	Peloponnese	Achaia	2020
12	KOR_ACH_06	Koroneiki	Peloponnese	Achaia	2020
13	KOR_ACH_07	Koroneiki	Peloponnese	Achaia	2020
14	KOR_ACH_08	Koroneiki	Peloponnese	Achaia	2020
15	KOR_ACH_09	Koroneiki	Peloponnese	Achaia	2020
16	KOR_ACH_10	Koroneiki	Peloponnese	Achaia	2020
17	KOR_CHA_14	Koroneiki	Crete	Chania	2020
18	KOR_CHA_15	Koroneiki	Crete	Chania	2020
19	KOR_CHA_16	Koroneiki	Crete	Chania	2020
20	KOR_CHA_17	Koroneiki	Crete	Chania	2020
21	KOR_CHA_18	Koroneiki	Crete	Chania	2020
22	KOR_CHA_19	Koroneiki	Crete	Chania	2020
23	KOR_CHA_20	Koroneiki	Crete	Chania	2020
24	KOR_EL_01	Koroneiki	Peloponnese	Ilia	2020
25	KOR_EL_02	Koroneiki	Peloponnese	Ilia	2020
26	KOR_EL_03	Koroneiki	Peloponnese	Ilia	2020
27	KOR_EL_04	Koroneiki	Peloponnese	Ilia	2020
28	KOR_EL_05	Koroneiki	Peloponnese	Ilia	2020
29	KOR_EL_06	Koroneiki	Peloponnese	Ilia	2020
30	KOR_EL_07	Koroneiki	Peloponnese	Ilia	2020
31	KOR_EL_08	Koroneiki	Peloponnese	Ilia	2020
32	KOR_EL_09	Koroneiki	Peloponnese	Ilia	2020
33	KOR_EL_10	Koroneiki	Peloponnese	Ilia	2020
34	KOR_EL_11	Koroneiki	Peloponnese	Ilia	2020
35	KOR_HER_13	Koroneiki	Crete	Heraklion	2020
36	KOR_HER_14	Koroneiki	Crete	Heraklion	2020
37	KOR_HER_15	Koroneiki	Crete	Heraklion	2020
38	KOR_HER_16	Koroneiki	Crete	Heraklion	2020
39	KOR_HER_17	Koroneiki	Crete	Heraklion	2020
40	KOR_HER_18	Koroneiki	Crete	Heraklion	2020
41	KOR_HER_19	Koroneiki	Crete	Heraklion	2020
42	KOR_HER_20	Koroneiki	Crete	Heraklion	2020
43	KOR_HER_21	Koroneiki	Crete	Heraklion	2020

	Sample Coding	Variety	Region	Sub-region	Harvesting Year
44	KOR_HER_22	Koroneiki	Crete	Heraklion	2020
45	KOR_HER_23	Koroneiki	Crete	Heraklion	2020
46	KOR_HER_24	Koroneiki	Crete	Heraklion	2020
49	KOR_LAS_08	Koroneiki	Crete	Lasithi	2020
50	KOR_LAS_09	Koroneiki	Crete	Lasithi	2020
51	KOR_LAS_10	Koroneiki	Crete	Lasithi	2020
52	KOR_LAS_11	Koroneiki	Crete	Lasithi	2020
53	KOR_LAS_12	Koroneiki	Crete	Lasithi	2020
54	KOR_LAS_13	Koroneiki	Crete	Lasithi	2020
55	KOR_LAS_14	Koroneiki	Crete	Lasithi	2020
56	KOR_LAS_15	Koroneiki	Crete	Lasithi	2020
57	KOR_MES_13_MAIX	Koroneiki	Peloponnese	Messenia	2020
58	KOR_MES_5_MAIX	Koroneiki	Peloponnese	Messenia	2020
59	KOR_MES_7_MAIX	Koroneiki	Peloponnese	Messenia	2020
60	KOR_MES_9_MAIX	Koroneiki	Peloponnese	Messenia	2020
61	KOR_RET_09	Koroneiki	Crete	Rethymno	2020
62	KOR_RET_10	Koroneiki	Crete	Rethymno	2020
63	KOR_RET_11	Koroneiki	Crete	Rethymno	2020
64	KOR_RET_12	Koroneiki	Crete	Rethymno	2020
65	KOR_RET_13	Koroneiki	Crete	Rethymno	2020
66	KOR_RET_14	Koroneiki	Crete	Rethymno	2020
67	KOR_RET_15	Koroneiki	Crete	Rethymno	2020
68	ADR_LES_19	Adramytini	Lesvos	Lesvos	2019
69	ADR_LES_27	Adramytini	Lesvos	Lesvos	2019
70	ADR_LES_28	Adramytini	Lesvos	Lesvos	2019
71	ADR_LES_29	Adramytini	Lesvos	Lesvos	2019
72	ADR_LES_30	Adramytini	Lesvos	Lesvos	2019
73	ADR_LES_31	Adramytini	Lesvos	Lesvos	2019
74	ADR_LES_32	Adramytini	Lesvos	Lesvos	2019
75	KOL_LES_17	Kolovi	Lesvos	Lesvos	2019
76	KOL_LES_18	Kolovi	Lesvos	Lesvos	2019
77	KOL_LES_20	Kolovi	Lesvos	Lesvos	2019
78	KOL_LES_21	Kolovi	Lesvos	Lesvos	2019
79	KOL_LES_22	Kolovi	Lesvos	Lesvos	2019
80	KOL_LES_23	Kolovi	Lesvos	Lesvos	2019
81	KOL_LES_24	Kolovi	Lesvos	Lesvos	2019
82	KOL_LES_25	Kolovi	Lesvos	Lesvos	2019
83	KOL_LES_26	Kolovi	Lesvos	Lesvos	2019
84	KOL_LES_33	Kolovi	Lesvos	Lesvos	2019
85	KOL_LES_34	Kolovi	Lesvos	Lesvos	2019
86	KOL_LES_35	Kolovi	Lesvos	Lesvos	2019
87	KOL_LES_36	Kolovi	Lesvos	Lesvos	2019
88	KOL_LES_37	Kolovi	Lesvos	Lesvos	2019
89	KOL_LES_38	Kolovi	Lesvos	Lesvos	2019
90	KOL_LES_39	Kolovi	Lesvos	Lesvos	2019
91	KOL_LES_40	Kolovi	Lesvos	Lesvos	2019

	Sample Coding	Variety	Region	Sub-region	Harvesting Year
92	KOL_LES_41	Kolovi	Lesvos	Lesvos	2019
93	KOL_LES_42	Kolovi	Lesvos	Lesvos	2019
94	KOL_LES_43	Kolovi	Lesvos	Lesvos	2019
95	KOL_LES_44	Kolovi	Lesvos	Lesvos	2019
96	KOL_LES_45	Kolovi	Lesvos	Lesvos	2019
97	KOL_LES_46	Kolovi	Lesvos	Lesvos	2019
98	KOL_LES_47	Kolovi	Lesvos	Lesvos	2019
99	KOL_LES_48	Kolovi	Lesvos	Lesvos	2019
100	KOL_LES_49	Kolovi	Lesvos	Lesvos	2019
101	KOR_CHA_10	Koroneiki	Crete	Chania	2019
102	KOR_CHA_11	Koroneiki	Crete	Chania	2019
103	KOR_CHA_12	Koroneiki	Crete	Chania	2019
104	KOR_CHA_13	Koroneiki	Crete	Chania	2019
105	KOR_KOR_01	Koroneiki	Peloponnese	Korinthos	2019
106	KOR_KOR_02	Koroneiki	Peloponnese	Korinthos	2019
107	KOR_KOR_03	Koroneiki	Peloponnese	Korinthos	2019
108	KOR_KOR_04	Koroneiki	Peloponnese	Korinthos	2019
109	KOR_KOR_05	Koroneiki	Peloponnese	Korinthos	2019
110	KOR_MES_13	Koroneiki	Peloponnese	Messenia	2019
111	KOR_MES_14	Koroneiki	Peloponnese	Messenia	2019
112	KOR_MES_15	Koroneiki	Peloponnese	Messenia	2019
113	KOR_MES_16	Koroneiki	Peloponnese	Messenia	2019
114	KOR_MES_17	Koroneiki	Peloponnese	Messenia	2019
115	KOR_MES_18	Koroneiki	Peloponnese	Messenia	2019
116	KOR_MES_19	Koroneiki	Peloponnese	Messenia	2019
117	KOR_MES_20	Koroneiki	Peloponnese	Messenia	2019
118	KOR_MES_21	Koroneiki	Peloponnese	Messenia	2019
119	KOR_MES_22	Koroneiki	Peloponnese	Messenia	2019
120	KOR_MES_23	Koroneiki	Peloponnese	Messenia	2019
121	KOR_MES_24	Koroneiki	Peloponnese	Messenia	2019
122	KOR_MES_25	Koroneiki	Peloponnese	Messenia	2019
123	KOR_MES_26	Koroneiki	Peloponnese	Messenia	2019
124	KOR_MES_27	Koroneiki	Peloponnese	Messenia	2019
125	KOR_MES_28	Koroneiki	Peloponnese	Messenia	2019
126	KOR_MES_29	Koroneiki	Peloponnese	Messenia	2019
127	KOR_MES_30	Koroneiki	Peloponnese	Messenia	2019
128	KOR_MES_31	Koroneiki	Peloponnese	Messenia	2019
129	KOR_MES_32	Koroneiki	Peloponnese	Messenia	2019

Table S2: Volatile composition of EVOOs according to the olive tree cultivar. The values represent the mean content (%) of the samples in each variety. Data in the same row with different lowercase letters differ significantly ($p < 0.05$). ADR: Adramytini variety; KOL: Kolovi variety; KOR: Koroneiki variety

Compound	Content (% of Total Identified Compounds)			RID ¹	
	ADR	KOL	KOR		
<i>Acids</i>					
Acetic acid	10.98 ^a	4.22 ^b	3.75 ^b	A	
Propanoic acid	0.18 ^a	0.11 ^a	0.18 ^a	A	
Butanoic acid	0.08 ^a	0.17 ^a	0.18 ^a	A	
3-Methylbutanoic acid	0.07 ^a	0.04 ^b	0.03 ^b	B	
Hexanoic acid	0.23 ^a	0.22 ^a	0.27 ^a	A	
2-Ethylhexanoic acid	0.11 ^a	0.08 ^a	0.07 ^a	B	
Heptanoic acid	0.05 ^{ab}	0.04 ^a	0.06 ^b	B	
Octanoic acid	0.13 ^a	0.07 ^b	0.08 ^b	A	
Nonanoic acid	0.56 ^a	0.22 ^b	0.38 ^a	B	
<i>Alcohols</i>					
Ethanol	4.82 ^a	3.80 ^a	4.63 ^a	A	
1-Propanol	0.06 ^a	0.03 ^b	0.02 ^c	A	
2-Methyl-1-propanol	0.60 ^a	0.22 ^b	0.10 ^c	A	
3-Pentanol	0.83 ^a	0.55 ^a	0.42 ^a	A	
1-Butanol	0.07 ^a	0.15 ^a	0.09 ^a	A	
1-Penten-3-ol	9.57 ^{ab}	7.45 ^a	10.78 ^b	A	
3-Methyl-1-butanol	1.55 ^a	0.39 ^b	0.17 ^c	A	
1-Pentanol	0.71 ^a	0.55 ^a	0.34 ^b	A	
(Z)-2-Penten-1-ol	2.41 ^a	3.34 ^a	4.16 ^b	B	
1-Hexanol	8.15 ^a	7.94 ^a	4.46 ^b	A	
(E)-3-Hexen-1-ol	0.38 ^a	0.26 ^a	0.28 ^a	B	
(Z)-3-Hexen-1-ol	7.94 ^{ab}	10.96 ^a	7.83 ^b	B	
(E)-2-Hexen-1-ol	10.15 ^a	5.83 ^a	6.09 ^a	B	
2-Ethyl-1-hexanol	1.05 ^a	0.56 ^b	0.23 ^c	B	
1-Octanol	0.08 ^{ab}	0.09 ^a	0.12 ^b	A	
1-Nonanol	0.05 ^{ab}	0.04 ^a	0.09 ^b	B	
Benzyl alcohol	0.08 ^a	0.09 ^a	0.15 ^b	A	
Phenethyl alcohol	0.26 ^a	0.25 ^a	0.46 ^b	A	
<i>Aldehydes</i>					
2-Methylbutanal	1.29 ^a	0.64 ^b	0.43 ^b	B	
3-Methylbutanal	0.42 ^a	0.27 ^a	0.21 ^a	B	
Pentanal	0.63 ^a	0.62 ^a	0.83 ^a	B	
Hexanal	0.67 ^a	0.93 ^a	1.46 ^b	A	
(E)-2-Pentenal	0.06 ^a	0.21 ^a	0.37 ^b	B	
(Z)-3-Hexenal	0.07 ^a	0.45 ^b	0.54 ^b	B	
(E)-3-Hexenal	0.24 ^a	2.96 ^{ab}	3.17 ^b	B	
Heptanal	0.03 ^a	0.05 ^a	0.12 ^b	B	
(E)-2-Hexenal	0.30 ^a	0.98 ^a	2.01 ^b	B	
Octanal	0.03 ^a	0.05 ^a	0.11 ^b	B	
Nonanal	0.23 ^a	0.33 ^a	0.79 ^b	B	
(E,E)-2,4-Hexadienal	0.21 ^a	0.62 ^a	0.44 ^b	B	
Benzaldehyde	0.09 ^{ab}	0.08 ^a	0.10 ^b	A	
(E)-4-Oxohex-2-enal	0.18 ^a	1.19 ^a	1.41 ^a	B	
<i>Esters</i>					
Methyl acetate	1.23 ^a	0.61 ^b	0.34 ^c	A	

Compound	Content (% of Total Identified Compounds)			RID ¹
	ADR	KOL	KOR	
Ethyl acetate	9.35 ^a	4.15 ^b	3.08 ^b	A
Hexyl acetate	0.20 ^a	1.36 ^b	2.74 ^c	A
(Z)-3-Hexenyl acetate	0.58 ^a	4.46 ^b	10.49 ^c	B
Methylbenzoate	0.01 ^a	0.01 ^a	0.05 ^b	B
Methylsalicylate	0.16 ^a	0.14 ^a	0.10 ^b	B
Methyl 2-oxohexanoate	0.23 ^a	1.22 ^a	0.98 ^{ab}	C
<i>Hydrocarbons</i>				
Benzene	0.07 ^a	0.13 ^a	0.21 ^a	B
n-Octane	0.16 ^a	0.22 ^a	0.29 ^a	A
3-Ethyl-1,5-octadiene (isomer 1)	1.05 ^a	1.40 ^a	2.21 ^b	B
3-Ethyl-1,5-octadiene (isomer 2)	0.34 ^a	0.49 ^a	0.83 ^b	B
4-Methyl-2,6-Octadiene	2.45 ^a	4.21 ^a	3.64 ^a	C
3-Ethyl-1,4-hexadiene	0.05 ^a	0.07 ^a	0.19 ^b	C
<i>Ketones</i>				
2-Butanone	0.07 ^a	0.06 ^a	0.10 ^a	B
3-Pentanone	15.62 ^a	15.77 ^a	10.38 ^b	B
1-Penten-3-one	1.03 ^a	7.16 ^b	3.40 ^a	B
2-Heptanone	0.04 ^a	0.09 ^a	0.09 ^a	B
Acetoin	0.34 ^a	0.26 ^a	0.21 ^a	A
2-Octanone	0.04 ^a	0.08 ^a	0.10 ^a	B
6-Methyl-5-hepten-2-one	0.12 ^a	0.09 ^b	0.12 ^a	B
<i>Terpenoids</i>				
α -Pinene	0.11 ^a	0.09 ^a	0.10 ^a	A
D-Limonene	0.03 ^a	0.07 ^a	0.05 ^a	A
beta-Ocimene	0.25 ^a	0.17 ^a	0.18 ^a	B
p-Cymene	0.02 ^a	0.02 ^a	0.03 ^a	A
(E)-4,8-Dimethylnona-1,3,7-triene	0.25 ^a	0.23 ^a	2.34 ^b	C
α -Farnesene	0.40 ^a	0.15 ^b	0.04 ^c	B
<i>Miscellaneous</i>				
2-Methylfuran	0.02 ^a	0.03 ^a	0.06 ^b	B
2-Ethylfuran	0.07 ^a	0.12 ^a	0.11 ^a	B
Guaiacol (2-Methoxyphenol)	0.02 ^a	0.02 ^a	0.02 ^a	B
Phenol	0.06 ^a	0.06 ^a	0.06 ^a	A
Dimethyl sulfide	0.01 ^a	0.06 ^a	0.04 ^a	B

¹ RID: reliability of identification was set at three levels; A-level: agreement of retention index (RI) and mass spectrum with those of an authentic compound; B-level: difference of experimental RI to literature RI < 20 and mass spectrum similarity match > 900; C-level: at least mass spectrum similarity match > 800 [20].

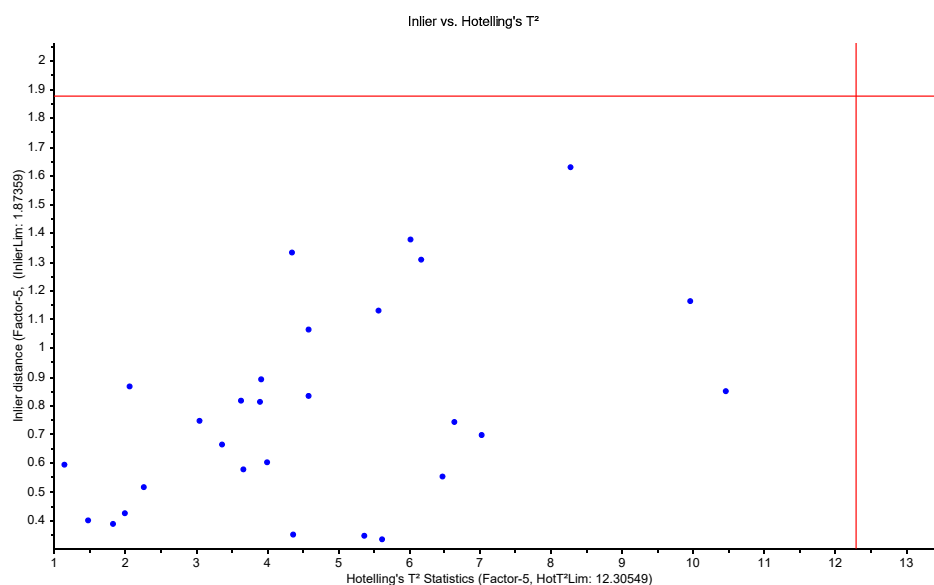


Figure S3: Inliers vs Hotelling's T2 plot of the predicted olive oil samples (blue dots) used in external validation of PLS-DA model. The associated critical limits (with a p-value of 5%) are displayed as horizontal and vertical red lines.

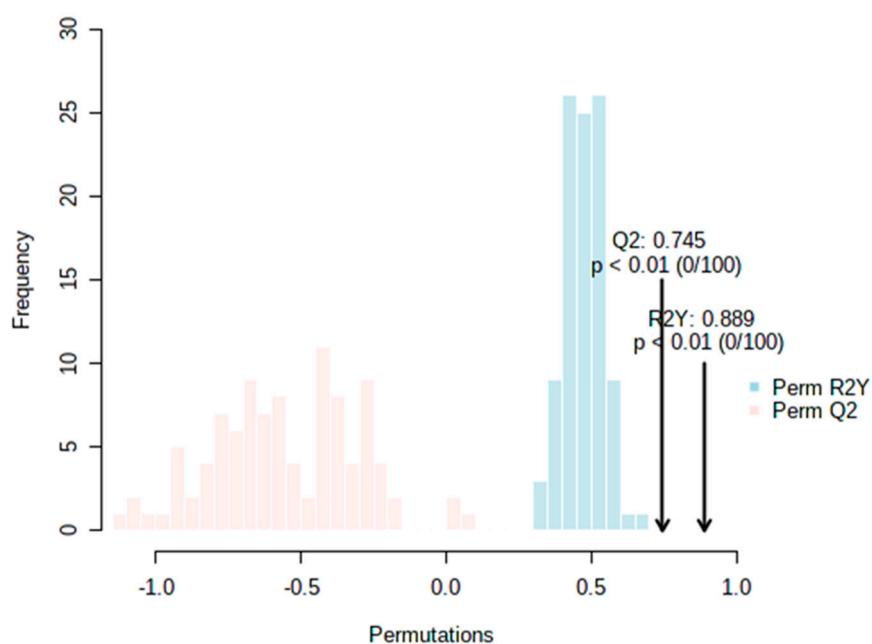
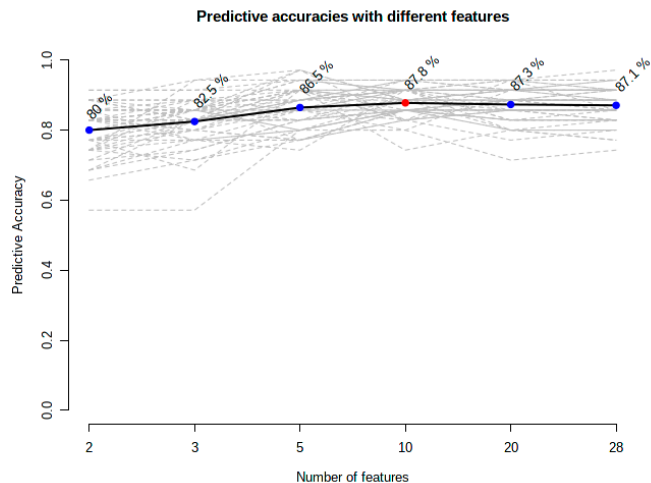
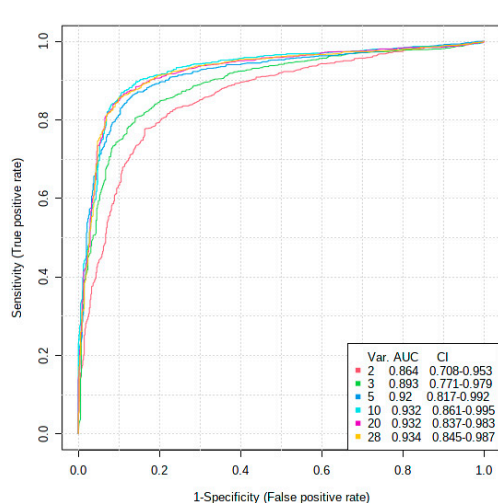
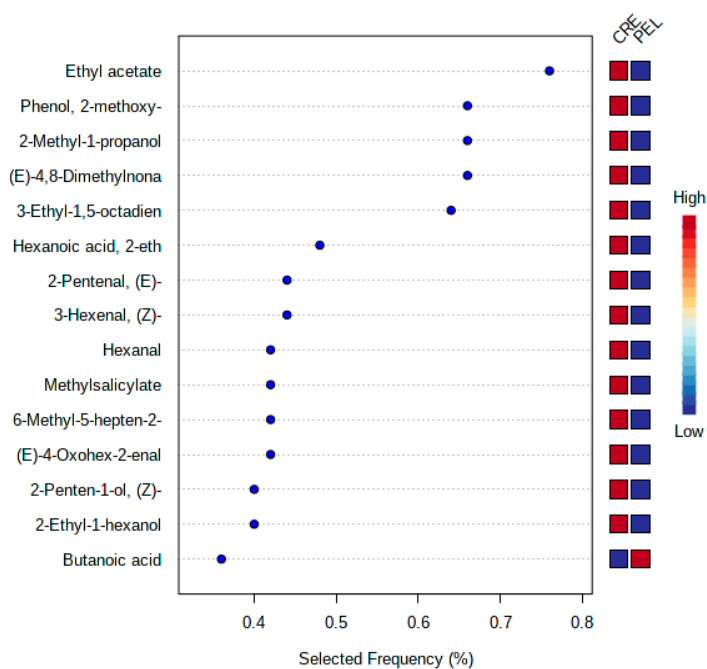


Figure S4: Permutation test of the OPLS-DA model



(a)

(b)



(c)

Figure S5: (a) ROC curves of all models resulted from the automated combination of 2, 3, 5, 10, 20 and 28 volatile compounds. The legend presents the AUC value and the corresponding confidence limits – CI for each model; (b) Plot of the predicted accuracies of each model with an increasing number of features (volatile compounds). The most accurate model is highlighted with a red dot; (c) Plot of the most important features of the selected model, ranked from most important to least important