

Supplementary Materials

Analysis of the Volatile Organic Compounds fingerprint of Greek grape marc spirits of various origins and traditional production styles

Maria Marinaki^{1,2,3}, Ioannis Sampsonidis^{3,4}, Alexandros Nakas^{5,6}, Panagiotis Arapitsas^{7,8*}, Andreana Assimopoulou^{5,6}, Georgios Theodoridis^{1,2,3*}

¹ Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; mmarinaki@chem.auth.gr

² Biomic_Auth, Bioanalysis and Omics Laboratory, CIRI-AUTH, 57001 Thessaloniki, Greece

³ FoodOmicsGR_Research Infrastructure, Auth Node, CIRI-AUTH, 57001 Thessaloniki, Greece; isampson@nutr.teithe.gr

⁴ Department of Nutritional Sciences & Dietetics, International Hellenic University, 57001 Thessaloniki, Greece

⁵ Laboratory of Organic Chemistry, School of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; anakas@cheng.auth.gr (A.N.); adreana@cheng.auth.gr (A.N.A.)

⁶ Natural Products Research Centre of Excellence (NatPro-AUTH), CIRI-AUTH, 57001 Thessaloniki, Greece

⁷ Department of Wine, Vine and Beverage Sciences, School of Food Science, University of West Attica, 12243 Athens, Greece; parapitsas@uniwa.gr

⁸ Research and Innovation Centre, Fondazione Edmund Mach, 38010 Trento, Italy; panagiotis.arapitsas@fmach.it

*Correspondence: gtheodor@chem.auth.gr, panagiotis.arapitsas@fmach.it

Table S1. Sample number, region, grape variety and addition of aromatic material of the analyzed samples.

Sample Number	Region	Grape variety	Addition of aromatic material
1	South Aegean, Crete Island	Liatiko	no
2	South Aegean, Crete Island	Liatiko	no
3	South Aegean, Crete Island	Liatiko-Kotsifali	no
4	South Aegean, Crete Island	Liatiko-Kotsifali	no
5	South Aegean, Crete Island	Liatiko-Mandilari	no
6	South Aegean, Crete Island	Soultanina	yes
7	South Aegean, Crete Island	Soultanina	no
8	South Aegean, Crete Island	Soultanina	no
9	South Aegean, Crete Island	Soultanina	no
10	South Aegean, Crete Island	Soultanina	no
11	South Aegean, Crete Island	Soultanina	no
12	South Aegean, Crete Island	Soultanina	no
13	South Aegean, Crete Island	Soultanina	no
14	South Aegean, Crete Island	Soultanina	no
15	South Aegean, Crete Island	Soultanina	no
16	South Aegean, Crete Island	Soultanina	no
17	South Aegean, Crete Island	Soultanina-Liatiko-Kotsifali	no
18	South Aegean, Crete Island	Soultanina-Liatiko-Kotsifali	no
19	South Aegean, Crete Island	Soultanina- Kotsifali-Cabernet	no
20	South Aegean, Crete Island	Soultanina-Liatiko-Mandilari	no
21	South Aegean, Crete Island	Soultanina-Kotsifali-Mandilari	no
22	South Aegean, Crete Island	Soultanina-Kotsifali-Mandilari	no
23	South Aegean, Crete Island	Liatiko-Mandilari	no
24	South Aegean, Crete Island	Liatiko-Mandilari	no
25	South Aegean, Crete Island	Mandilari-Syrah-Cabernet	yes
26	South Aegean, Crete Island	Soultanina-Muscat	no
27	South Aegean, Crete Island	Syrah	no
28	Macedonia, Thessaloniki	Muscat	yes
29	Macedonia, Thessaloniki	Muscat	yes
30	Macedonia, Thessaloniki	Muscat	yes
31	Macedonia, Thessaloniki	Muscat	yes
32	Macedonia, Thessaloniki	Muscat	no
33	Macedonia, Thessaloniki	Muscat-Roditis-Merlot	yes
34	Macedonia, Thessaloniki	Muscat-Roditis-Merlot	yes
35	Macedonia, Thessaloniki	Muscat-Roditis-Merlot	yes
36	Macedonia, Pella	Merlot-Grand noir-Cabernet	no
37	Macedonia, Pella	Merlot-Grand noir-Cabernet	no
38	Macedonia, Pella	Merlot-Grand noir-Cabernet	no
39	Macedonia, Pella	Merlot-Grand noir-Cabernet	no
40	Macedonia, Kavala	Soultanina	yes
41	Macedonia, Kilkis	Muscat	yes
42	Macedonia, Nea Mesimvria	Muscat	yes
43	Macedonia, Litohoro	Muscat	yes
44	Macedonia, Serres	Muscat	yes
45	Macedonia, Serres	Muscat	yes
46	Macedonia, Serres	Muscat	yes
47	Macedonia, Serres	Muscat-Cabernet	yes

48	Thessaly, Tyrnavos	Muscat	yes
49	Thessaly, Larissa	Muscat	yes
50	Thessaly, Tyrnavos	Muscat-Cabernet	yes
51	Cyprus	Soultanina	no
52	North Aegean, Limnos Island	Muscat of Alexandria	yes
53	North Aegean, Limnos Island	Muscat of Alexandria	yes
54	North Aegean, Limnos Island	Muscat of Alexandria	yes
55	North Aegean, Limnos Island	Muscat of Alexandria	yes
56	North Aegean, Limnos Island	Muscat of Alexandria	yes
57	North Aegean, Limnos Island	Muscat of Alexandria	yes
58	North Aegean, Limnos Island	Muscat of Alexandria	yes
59	North Aegean, Limnos Island	Muscat of Alexandria	yes
60	North Aegean, Limnos Island	Muscat of Alexandria	yes

Table S2. Compound name, retention time (RT), chemical formula, molecular weight (MR) and relative concentration (mg L⁻¹) according to the production region of the metabolites identified in analyzed Greek distillates

Compound name	RT (min)	Chemical Formula	MR	Crete	Thessaloniki	Limnos	Pella	Serres	Thessaly	Cyprus	Kavala	Kilkis	Nea Mesimvria	Litohoro
ACIDS				mg L ⁻¹ ± sd						mg L ⁻¹				
Acetic acid	16.82	C2H4O2	60.05	3.61±2.51	6.26±3.32	0.67±0.54	2.63±0.42	3.49±5.88	10.53±17.38	5.80	1.19	10.30	1.29	2.04
Octanoic acid	38.44	C8H16O2	144.21	0.05±0.04	0.66±1.61	0.64±1.44	0.04±0.01	0.07±0.03	9.15±15.00	0.07	0.07	0.11	0.01	0.04
Decanoic acid	43.29	C10H20O2	172.26	0.14±0.50	4.21±11.41	2.44±5.83	0.02±0.01	0.18±0.32	8.98±15.43	0.02	0.02	0.04	0.01	0.02
ALCOHOLS														
2-Methylpropan-1-ol	4.33	C4H10O	74.12	6.86±2.91	13.33±5.29	11.08±2.23	7.38±0.41	11.60±3.42	6.90±11.09	27.04	13.36	19.21	21.34	9.51
1-Butanol	5.45	C4H10O	74.12	0.44±0.23	0.44±0.07	0.45±0.18	0.40±0.04	0.33±0.10	0.19±0.24	9.23	0.31	0.29	0.38	0.55
Isoamyl alcohol	7.19	C5H12O	88.15	56.17±25.03	66.97±19.72	76.41±14.74	50.13±6.60	91.75±28.54	33.25±38.69	235.27	74.16	137.10	162.54	99.80
1-Hexanol	12.50	C6H14O	102.17	1.11±0.58	1.85±1.49	1.10±0.27	0.33±0.07	1.05±0.42	1.18±0.54	2.42	1.69	2.97	1.82	1.85
1-Heptanol	16.69	C7H16O	116.20	0.07±0.03	0.10±0.08	0.11±0.02	0.06±0.01	0.06±0.02	0.10±0.09	0.15	0.09	0.07	0.11	0.17
cis-Hept-4-enol	18.64	C7H14O	114.18	0.05±0.16	0.06±0.07	0.22±0.12	0.04±0.01	0.11±0.19	0.03±0.02	0.03	0.31	0.04	0.04	0.04
1-Octanol	20.83	C8H18O	130.22	0.09±0.05	0.09±0.04	0.08±0.03	0.06±0.02	0.06±0.02	0.15±0.17	0.13	0.09	0.10	0.08	0.13
2,6-dimethyl-3,7-Octadiene-2,6-diol	29.09	C10H18O2	170.25	0.00±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.01	0.05±0.07	0.01	0.01	0.00	0.00	0.01
2-Phenylethanol	33.52	C8H10O	122.16	12.86±6.78	7.20±3.15	10.03±14.93	6.65±1.16	8.08±5.50	16.13±14.65	10.23	10.28	22.70	7.10	15.39
CARBONYL COMPOUNDS														
Acetaldehyde	1.34	C2H4O	44.05	1.30±0.72	1.14±0.51	1.26±0.63	0.78±0.20	1.34±0.70	2.10±3.64	0.33	0.55	1.83	0.40	1.31
2-Heptanone	1.62	C7H14O	114.19	0.14±0.13	0.27±0.21	0.23±0.14	0.08±0.01	3.01±4.95	0.14±0.23	0.44	0.16	0.14	1.62	0.41
Acetaldehyde ethyl methyl acetal	1.74	C5H12O2	104.15	1.10±0.58	0.94±0.40	0.24±0.24	0.67±0.12	0.52±0.59	1.63±2.80	0.12	0.26	1.59	0.25	1.31
Isovaleraldehyde diethyl acetal	4.05	C9H20O2	160.25	0.27±0.20	1.15±0.96	0.45±0.31	0.15±0.01	0.55±0.8	0.10±0.18	0.22	0.24	0.38	0.13	0.85
Acetaldehyde ethyl amyl acetal	4.66	C9H20O2	160.25	0.32±0.21	0.28±0.13	0.34±0.22	0.13±0.03	0.43±0.33	0.47±0.81	0.11	0.17	1.01	0.38	0.65
3-Ethoxypropanal diethyl acetal	10.67	C9H20O3	176.25	0.03±0.02	0.06±0.04	0.02±0.01	0.03±0.01	0.03±0.03	0.02±0.01	0.07	0.03	0.05	0.03	0.02
Nonanal	14.07	C9H18O	142.24	0.05±0.03	0.06±0.03	0.11±0.03	0.03±0.01	0.09±0.06	0.03±0.03	0.06	0.08	0.08	0.10	0.07
Furfural	16.98	C5H4O2	96.08	1.12±0.70	0.88±0.15	1.18±0.46	0.43±0.12	0.68±0.26	0.14±0.11	11.58	0.55	0.54	0.42	1.32
Benzaldehyde	19.05	C7H6O	106.12	0.85±0.52	1.48±0.96	0.83±0.19	0.52±0.08	0.49±0.18	0.27±0.23	3.18	1.76	1.08	0.28	0.75
Nonanal diethyl acetal	19.67	C13H28O2	216.36	0.06±0.05	0.12±0.12	0.15±0.09	0.04±0.02	0.21±0.30	0.06±0.05	0.08	0.15	0.13	0.12	0.12
4-Anisaldehyde	36.90	C8H8O2	136.15	4.21±14.42	18.88±47.07	22.11±33.42	0.54±0.36	18.13±22.29	11.95±19.58	0.02	0.42	9.70	0.05	0.08
2-Allyl-1,4-dimethoxybenzene	37.57	C11H14O2	178.22	0.03±0.09	0.03±0.06	0.48±0.40	0.02±0.01	0.05±0.07	0.03±0.03	0.00	0.00	0.01	0.00	0.00

2-(4-Hexyl-2,5-dioxofuran-3-yl)acetic acid	39.09	C12H16O5	240.25	0.06±0.11	0.54±1.19	0.81±1.06	0.02±0.01	0.10±0.11	0.94±1.52	0.08	0.08	0.05	0.01	0.02
<i>p</i> -Anisaldehyde diethyl acetal	42.01	C10H14O3	182.22	0.37±1.36	8.97±24.11	5.16±13.22	0.02±0.01	0.70±0.99	17.65±30.54	0.00	0.01	0.15	0.00	0.00
ESTERS														
Methyl acetate	1.67	C3H6O2	74.08	0.27±0.21	0.43±0.28	0.47±0.23	0.20±0.03	0.91±1.16	0.56±0.97	0.34	0.45	0.38	0.56	0.45
Ethyl Acetate	1.96	C4H8O2	88.11	82.12±48.94	119.76±90.71	137.48±85.36	61.66±8.39	223.49±320.78	205.49±353.79	55.55	130.87	215.48	27.99	61.87
Ethyl butyrate	3.43	C6H12O2	116.16	1.39±2.09	0.38±0.16	0.39±0.20	0.60±0.08	0.68±0.30	0.37±0.61	4.99	0.56	0.40	1.15	0.90
Ethyl 2-methylbutanoate	3.65	C7H14O2	130.18	0.34±0.22	0.10±0.05	0.20±0.15	0.06±0.01	0.14±0.09	0.12±0.18	0.15	0.07	0.79	0.53	0.22
Ethyl isovalerate	3.92	C7H14O2	130.18	0.35±0.25	0.16±0.10	0.03±0.01	0.06±0.01	0.12±0.2	0.27±0.44	0.18	0.05	1.18	0.04	0.20
Isoamyl acetate	4.99	C7H14O2	130.18	1.63±0.89	2.34±0.70	2.91±0.81	1.35±0.05	4.13±3.64	2.87±4.76	3.26	2.52	7.02	2.20	2.42
Ethyl hexanoate	8.02	C8H16O2	144.21	2.96±1.36	2.97±1.28	2.48±1.23	2.42±0.41	3.07±1.86	1.94±2.88	2.23	4.37	4.50	2.80	6.96
Neryl hexanoate	11.31	C16H28O2	252.39	0.02±0.03	0.40±0.33	0.23±0.14	0.13±0.03	0.09±0.08	0.12±0.17	0.03	0.06	0.02	0.05	0.07
Ethyl heptanoate	11.75	C9H18O2	158.24	0.10±0.07	0.13±0.07	0.11±0.04	0.07±0.02	0.07±0.06	0.05±0.07	0.10	0.21	0.14	0.12	0.14
Ethyl lactate	12.12	C5H10O3	118.13	2.21±1.34	6.78±1.92	2.08±1.52	3.79±0.63	2.49±1.54	0.99±1.12	5.02	7.34	3.21	1.28	2.63
Ethyl octanoate	15.84	C10H20O2	172.26	20.81±25.95	38.35±10.48	14.65±5.78	29.77±5.45	30.26±20.85	15.52±25.47	21.99	76.68	43.26	31.43	6.45
Ethyl nonanoate	19.94	C11H22O2	186.29	0.42±0.39	1.00±1.01	0.27±0.15	0.31±0.07	0.23±0.16	0.18±0.25	0.32	0.71	0.57	0.37	0.12
Ethyl 2-hydroxy-4-methylvalerate	20.23	C8H16O3	160.21	0.03±0.02	0.13±0.13	0.04±0.01	0.03±0.01	0.04±0.02	0.05±0.06	0.09	0.09	0.06	0.05	0.02
Methyl 9-oxononanoate	22.23	C10H18O3	186.25	0.16±0.33	0.37±0.16	0.10±0.03	0.19±0.05	0.17±0.11	0.12±0.16	0.13	0.87	0.34	0.16	0.06
Ethyl decanoate	23.96	C12H24O2	200.32	36.31±66.69	88.10±39.22	38.50±15.99	80.86±21.21	54.55±29.96	25.37±37.18	56.49	25.68	125.02	41.81	11.74
3-Methylbutyl octanoate	24.67	C13H26O2	214.34	0.47±1.80	0.65±0.46	0.41±0.14	0.8±0.59	0.66±0.64	0.07±0.07	0.22	0.02	0.38	0.73	0.14
Ethyl phenylacetate	29.24	C10H12O2	164.20	0.09±0.13	0.35±0.48	0.17±0.08	0.06±0.02	0.21±0.24	0.37±0.35	0.17	0.63	0.20	0.14	0.22
Phenethyl acetate	30.26	C10H12O2	164.20	0.11±0.12	0.29±0.19	0.84±0.52	0.14±0.04	0.97±0.62	0.76±0.98	0.40	0.63	0.24	0.26	0.24
Ethyl dodecanoate	31.43	C14H28O2	228.37	3.91±8.47	10.80±6.80	12.12±5.90	9.94±4.96	7.49±6.16	2.41±1.80	6.53	30.77	10.63	1.47	3.44
Isoamyl decanoate	32.05	C15H30O2	242.40	0.12±0.37	0.20±0.17	0.27±0.22	0.22±0.22	0.19±0.22	0.06±0.07	0.10	0.99	0.10	0.05	0.10
Ethyl myristate	38.03	C16H32O2	256.42	0.07±0.16	0.38±0.48	0.47±0.37	0.14±0.12	0.18±0.18	0.14±0.21	0.06	0.57	0.07	0.00	0.07
Ethyl palmitate	42.83	C18H36O2	284.50	0.03±0.05	0.45±0.68	0.43±0.52	0.04±0.02	0.10±0.08	0.24±0.40	0.03	0.13	0.02	0.01	0.02
TERPENES AND TERPENOIDS														
<i>alpha</i> -Pinene	3.18	C10H16	136.23	0.06±0.27	0.02±0.02	0.44±0.60	0.01±0.00	49.64±99.24	0.00±0.00	0.01	2.87	0.00	0.00	0.06
<i>beta</i> -Myrcene	5.95	C10H16	136.23	0.02±0.04	0.05±0.03	0.25±0.21	0.03±0.01	15.04±30.06	0.04±0.06	0.00	1.53	0.02	0.01	0.02
D-Limonene	6.84	C10H16	136.23	0.29±1.19	1.26±0.62	0.24±0.09	0.25±0.10	90.05±179.91	0.32±0.54	0.01	45.24	1.85	0.09	1.24
4-Carene	8.28	C10H16	136.23	0.07±0.21	0.10±0.05	0.29±0.13	0.04±0.01	8.55±17.05	0.05±0.07	0.01	6.28	0.57	0.03	0.06
o-Cymene	9.17	C10H14	134.22	0.22±0.89	0.51±0.26	1.15±0.55	0.13±0.05	9.89±19.54	0.07±0.08	0.02	12.76	3.37	0.07	0.19
<i>alpha</i> -Terpinene	9.59	C10H16	136.23	0.02±0.04	0.19±0.14	0.08±0.05	0.05±0.01	2.02±4.02	0.11±0.15	0.01	0.67	0.13	0.02	0.03

<i>alpha</i> -Terpineol	16.05	C10H18O	154.25	0.14±0.12	1.66±1.28	0.29±0.15	0.52±0.08	1.42±2.48	1.94±3.22	0.38	1.17	2.85	0.12	0.58
Cedrene	16.54	C15H24	204.35	0.25±0.11	0.34±0.18	0.29±0.12	0.37±0.08	0.23±0.20	0.19±0.31	0.46	0.19	0.30	0.62	0.22
Nerol oxide	17.06	C10H16O	152.23	0.03±0.02	0.29±0.20	0.32±0.12	0.07±0.01	0.06±0.06	0.08±0.07	0.29	0.07	0.04	0.02	0.14
Ylangene	17.26	C15H24	204.35	0.11±0.39	0.08±0.11	1.09±0.65	0.03±0.01	0.22±0.42	0.01±0.01	0.01	0.48	0.04	0.04	0.01
<i>cis</i> -Sesquisabinene hydrate	17.60	C15H26O	222.36	0.02±0.03	0.11±0.07	0.13±0.04	0.04±0.01	0.08±0.10	0.14±0.23	0.05	0.11	0.05	0.01	0.06
2-Bornanone	18.38	C10H16O	152.23	0.01±0.01	0.02±0.01	0.05±0.03	0.01±0.00	0.14±0.26	0.05±0.07	0.02	0.29	0.05	0.01	0.03
Geraniol	18.93	C10H18O	154.25	0.04±0.03	0.38±0.24	0.22±0.10	0.12±0.03	0.07±0.06	0.72±1.14	0.09	0.08	0.14	0.03	0.11
Linalool	20.52	C10H18O	154.25	0.06±0.20	2.38±1.52	3.96±1.94	0.94±0.23	0.98±1.50	1.74±2.69	0.11	0.38	0.03	0.24	1.73
Caryophyllene	21.65	C15H24	204.35	0.06±0.13	0.04±0.01	0.41±0.24	0.05±0.01	0.27±0.48	0.04±0.03	0.06	0.30	0.06	0.07	0.05
Terpinen-4-ol	22.25	C10H18O	154.25	0.03±0.03	0.07±0.04	0.07±0.02	0.03±0.01	0.48±0.87	3.73±6.41	0.04	1.06	0.16	0.02	0.10
<i>trans</i> -Sesquisabinene hydrate	22.71	C15H26O	222.36	0.01±0.01	0.45±0.48	0.02±0.01	0.03±0.03	0.03±0.03	0.02±0.02	0.02	0.11	0.01	0.01	0.02
Hotrienol	22.95	C10H16O	152.23	0.01±0.01	0.22±0.15	1.76±1.05	0.12±0.03	0.19±0.28	0.22±0.33	0.01	0.08	0.01	0.03	0.21
<i>alpha</i> -Himachalene	23.28	C15H24	204.35	0.13±0.51	0.05±0.01	1.69±0.98	0.04±0.01	0.06±0.05	0.04±0.03	0.09	0.07	0.05	0.04	0.04
<i>gamma</i> -Himalachene	25.31	C15H24	204.35	3.98±19.12	0.40±0.80	38.65±21.78	0.39±0.24	1.57±2.94	0.67±1.09	0.02	0.10	0.09	0.02	0.02
<i>alpha</i> -Cedrene	25.94	C15H24	204.35	0.66±3.17	0.07±0.08	6.39±3.96	0.06±0.03	0.25±0.45	0.14±0.13	0.02	0.05	0.03	0.01	0.02
<i>alpha</i> -Zingiberene	26.77	C15H24	204.35	0.09±0.38	0.04±0.05	3.36±2.46	0.04±0.02	0.16±0.29	0.06±0.07	0.02	0.07	0.04	0.01	0.27
Isolongifolene	27.06	C15H24	202.33	0.05±0.21	0.02±0.03	1.51±0.93	0.02±0.01	0.02±0.04	0.07±0.07	0.01	0.02	0.01	0.01	0.01
<i>alpha</i> -Cadinene	27.90	C15H24	204.35	0.17±0.56	0.12±0.07	0.70±0.42	0.14±0.10	0.69±1.32	0.05±0.08	0.01	1.63	0.21	0.05	0.11
<i>alpha</i> -Curcumene	28.69	C15H22	202.34	0.81±3.93	0.05±0.08	2.82±1.55	0.06±0.04	0.56±1.03	0.06±0.11	0.01	0.04	0.02	0.01	0.01
<i>gamma</i> -Isogeraniol	29.45	C10H18O	154.25	0.01±0.01	0.02±0.01	0.02±0.01	0.02±0.00	0.01±0.01	0.06±0.09	0.01	0.01	0.01	0.01	0.02
4,5,9,10-dehydro-Isolongifolene	31.60	C15H20	200.32	0.03±0.11	0.01±0.00	0.05±0.02	0.01±0.00	0.01±0.00	0.05±0.04	0.00	0.01	0.01	0.00	0.00
<i>gamma</i> -Dehydro-ar-himachalene	32.77	C15H20	200.32	0.06±0.28	0.00±0.01	0.16±0.08	0.01±0.01	0.06±0.10	0.01±0.01	0.00	0.00	0.00	0.00	0.00
<i>beta</i> -Calacorene	33.35	C15H20	200.32	0.13±0.52	0.05±0.03	0.43±0.24	0.04±0.02	0.22±0.39	0.03±0.04	0.01	0.15	0.07	0.02	0.02
OTHERS														
epi-Nepeta lactone	3.78	C10H14O2	166.22	0.01±0.01	0.01±0.00	0.02±0.02	0.01±0.00	0.71±1.42	0.00±0.00	0.00	0.21	0.02	0.00	0.01
Mesitylene	8.25	C9H12	120.19	0.75±0.26	0.43±0.15	0.32±0.06	0.36±0.03	1.65±2.29	0.57±0.26	0.05	1.31	0.44	0.38	0.65
3-Acetylphenol	9.60	C8H8O2	136.15	0.02±0.04	0.22±0.17	0.09±0.05	0.06±0.02	2.07±4.11	0.14±0.19	0.02	0.69	0.17	0.02	0.03
Fenchone	13.79	C10H16O	152.23	0.01±0.01	0.03±0.02	0.03±0.01	0.01±0.00	13.85±27.55	0.16±0.25	0.03	34.89	3.60	0.02	0.02
1,3-Di-tert-butylbenzene	15.46	C14H22	190.32	0.01±0.02	0.01±0.01	0.02±0.03	0.01±0.00	10.45±7.94	0.02±0.02	0.01	0.01	0.00	16.35	9.12
Styrene	15.74	C8H8	104.15	0.01±0.01	0.08±0.05	0.02±0.01	0.03±0.00	0.18±0.30	0.03±0.02	0.01	0.25	0.21	0.03	0.02
Thymol methyl ether	19.38	C11H16O	164.24	0.02±0.01	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.05±0.07	0.12	0.01	0.02	0.01	0.01
Menthol	23.78	C10H20O	156.26	0.05±0.05	0.13±0.11	0.10±0.04	0.18±0.15	0.13±0.11	0.12±0.12	0.03	0.01	0.07	0.26	1.66
Estragole	24.91	C10H12O	148.20	1.95±8.24	0.68±0.16	27.33±9.26	0.14±0.06	31.10±60.84	0.45±0.19	0.03	2.94	22.45	0.35	9.96

Aromandendrene	26.40	C15H24	204.35	0.05±0.11	0.04±0.03	2.23±1.25	0.05±0.02	0.06±0.08	0.04±0.05	0.01	0.13	0.05	0.02	0.02
Carvone	26.91	C10H14O	150.22	0.05±0.22	0.02±0.02	0.36±0.72	0.01±0.00	1.36±2.68	0.86±1.16	0.01	0.70	1.57	0.01	2.18
<i>trans-p</i> -Mentha-1(7), 8-dien-2-ol	29.63	C10H16O	152.23	0.00±0.00	0.01±0.01	0.01±0.01	0.00±0.00	0.01±0.01	0.06±0.09	0.01	0.02	0.01	0.00	0.00
4,4-Dimethyl-3- (3-methylbut-3-enylidene) -2-methylene-bicyclo [4,1,0] heptane	30.17	C15H22	202.33	0.08±0.34	0.03±0.03	0.68±0.40	0.03±0.02	0.07±0.11	0.02±0.03	0.01	0.07	0.02	0.02	0.01
Anethole	30.64	C10H12O	148.20	71.77±253.90	36.24±44.19	1317.91±673.69	31.20±20.23	604.01±751.25	35.23±43.97	0.62	14.64	130.84	3.54	6.84
2,4-Di-tert-butylphenol	44.13	C14H22O	206.32	0.07±0.06	0.17±0.15	0.36±0.59	0.06±0.04	0.20±0.14	0.15±0.17	0.14	0.13	0.02	0.04	0.11

Table S3. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Crete-Soultanina and Macedonia Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Ethyl acetate	3.4693	0.5227	0.0297
Ethyl decanoate	3.2993	0.7166	3.33×10^{-8}
Isoamyl alcohol	2.0860	-0.5933	0.0336
Anethole	1.9373	0.5217	0.0154
Estragole	1.6440	-0.4977	0.0244
2-Phenylethanol	1.5368	-0.5890	0.0158
Ethyl octanoate	0.9902	0.4925	2.85×10^{-7}
Acetic acid	0.7771	0.5905	0.0343
Linalool	0.7000	0.6687	4.72×10^{-14}
D-Limonene	0.6631	-0.5153	5.61×10^{-14}
<i>alpha</i> -Terpineol	0.6449	0.6921	2.95×10^{-11}
Fenchone	0.6323	-0.5497	0.0214
Furfural	0.5605	-0.5539	0.0598
Ethyl lactate	0.5585	0.5092	1.85×10^{-7}
Ethyl dodecanoate	0.5559	0.5364	8.83×10^{-7}
2-Methylpropan-1-ol	0.5369	0.4960	0.0575
Isoamyl acetate	0.5117	0.5325	0.0062
Isovaleraldehyde diethyl acetal	0.5028	0.5803	0.0711
<i>o</i> -Cymene	0.5013	-0.4966	3.98×10^{-7}
Ethyl butyrate	0.5013	-0.5629	0.0301

Table S4. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Crete and Limnos Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Anethole	7.3356	0.9038	2.36×10^{-6}
<i>gamma</i> -Himalachene	1.2662	0.8370	6.90×10^{-6}
Ethyl acetate	1.2480	-0.5091	0.0251
Isoamyl alcohol	1.1911	-0.5357	0.0065
Estragole	1.0744	0.9073	7.27×10^{-9}
4-Anisaldehyde	0.9042	0.5725	0.0247
Ethyl octanoate	0.6793	-0.6096	0.0485
2-Phenylethanol	0.6621	-0.5580	0.0322
Ethyl dodecanoate	0.6053	0.7259	1.15×10^{-5}
<i>alpha</i> -Cedrene	0.5141	0.8004	2.10×10^{-5}

Table S5. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Macedonia and Limnos Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Anethole	7.0784	-0.8799	0.0014
Ethyl decanoate	1.6646	0.5899	0.0002
Ethyl octanoate	1.2598	0.8059	2.11×10^{-6}
<i>gamma</i> -Himalachene	1.2094	-0.7895	0.0026
Estragole	1.0191	-0.8709	7.69×10^{-5}
4-Anisaldehyde	0.8899	-0.5234	0.0145
Isoamyl alcohol	0.7035	0.5733	0.0191

Ethyl acetate	0.6811	0.5445	0.0135
Ethyl lactate	0.5930	0.8382	7.26×10^{-6}
Acetic acid	0.5285	0.7181	2.11×10^{-7}
<i>p</i> -Anisaldehyde diethyl acetal	0.5192	-0.5254	0.0261
<i>alpha</i> -Cedrene	0.5120	-0.7522	0.0047
2-Methylpropan-1-ol	0.5068	0.4914	0.0453
<i>n</i> -Decanoic acid	0.5039	-0.5516	0.02437
Ethyl dodecanoate	0.5034	0.5141	0.01198
<i>alpha</i> -Terpineol	0.4977	0.7347	5.42×10^{-9}
Aromandendrene	0.4932	-0.7919	0.0026
Benzaldehyde	0.4921	0.6821	3.41×10^{-7}
D-Limonene	0.4910	0.8087	3.32×10^{-8}

Table S6. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Crete and Thessaloniki Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Ethyl decanoate	3.5260	0.6994	0.0230
2-Phenylethanol	1.6494	-0.5932	0.0150
Ethyl octanoate	1.5087	0.4928	0.0367
4-Anisaldehyde	1.4975	0.5345	0.0817
Ethyl dodecanoate	1.4311	0.7455	0.0221
Ethyl acetate	1.1736	0.4931	0.0471
<i>p</i> -Anisaldehyde diethyl acetal	1.0809	0.5413	0.0343
Isoamyl alcohol	0.9599	-0.5287	0.0136
Anethole	0.8110	0.6974	0.0305
<i>n</i> -Decanoic acid	0.7505	0.5470	0.0344
2-Methylpropan-1-ol	0.6961	0.5343	4.40×10^{-5}
Linalool	0.6455	0.7107	3.09×10^{-9}
Ethyl lactate	0.6292	0.5025	5.96×10^{-9}
<i>alpha</i> -Terpineol	0.6280	0.6137	3.33×10^{-9}
D-Limonene	0.6648	0.6953	0.0173
Isoamyl octanoate	0.6590	0.7443	0.3888
Furfural	0.6322	-0.5380	0.0179
Ethyl myristate	0.6276	0.65495	0.0031
Ethyl palmitate	0.5968	0.6783	0.0014
Octanoic acid	0.5949	0.5672	0.0277
Ethyl nonanoate	0.5896	0.5918	0.0098

Table S7. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Thessaloniki and Limnos Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Anethole	7.1815	0.9915	4.04×10^{-5}
Ethyl decanoate	1.5870	-0.6093	0.0016
Ethyl octanoate	1.1235	-0.7635	1.54×10^{-5}
<i>gamma</i> -Himalachene	1.0226	0.7487	8.80×10^{-5}
Estragole	0.8615	0.8114	3.66×10^{-7}
Isoamyl alcohol	0.7614	-0.5639	0.0138
Ethyl acetate	0.5914	-0.5408	0.0421

Table S8. VIP, p(corr) and *p*-values of the statistically significant volatile metabolites of the discrimination between Thessaloniki and Pella Greek grape marc spirits.

Compound Name	VIP	p(corr)	<i>p</i> -value
Ethyl acetate	3.9473	-0.5959	0.0120
Ethyl decanoate	2.3594	-0.5874	0.0370
Isoamyl alcohol	2.3280	-0.5763	0.0067
Ethyl octanoate	1.8796	-0.5114	0.0480
4-Anisaldehyde	1.7609	-0.5202	0.0232
2-Methylpropan-1-ol	1.2745	-0.5320	0.0266
<i>p</i> -Anisaldehyde diethyl acetal	1.2176	-0.5090	0.0244
Anethole	1.1020	-0.7366	0.008
Acetic acid	0.8901	-0.5786	0.0300
Ethyl dodecanoate	0.8722	-0.5509	0.0414
Ethyl lactate	0.7877	-0.5723	0.0071
Isoamyl acetate	0.5921	-0.7284	0.0104
1-Hexanol	0.5573	-0.3510	0.0372
D-Limonene	0.5366	-0.7249	0.0050
Linalool	0.5329	-0.52164	0.0479
Ethyl hexanoate	0.5268	-0.5350	0.0216
<i>alpha</i> -Terpineol	0.5234	-0.6172	0.0471
Benzaldehyde	0.5188	-0.5785	0.0400

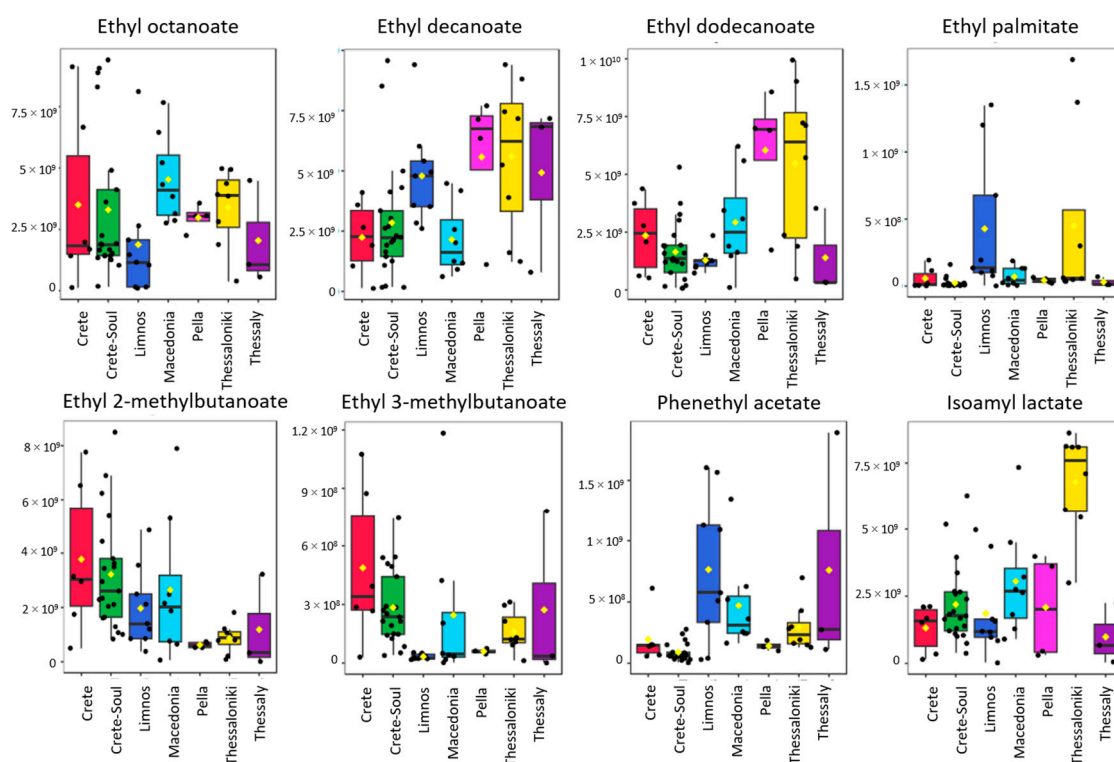


Figure S1. Boxplots of representative esters among Greek grape marc spirit samples. Black dots represent the samples' values and yellow dots are the mean values.

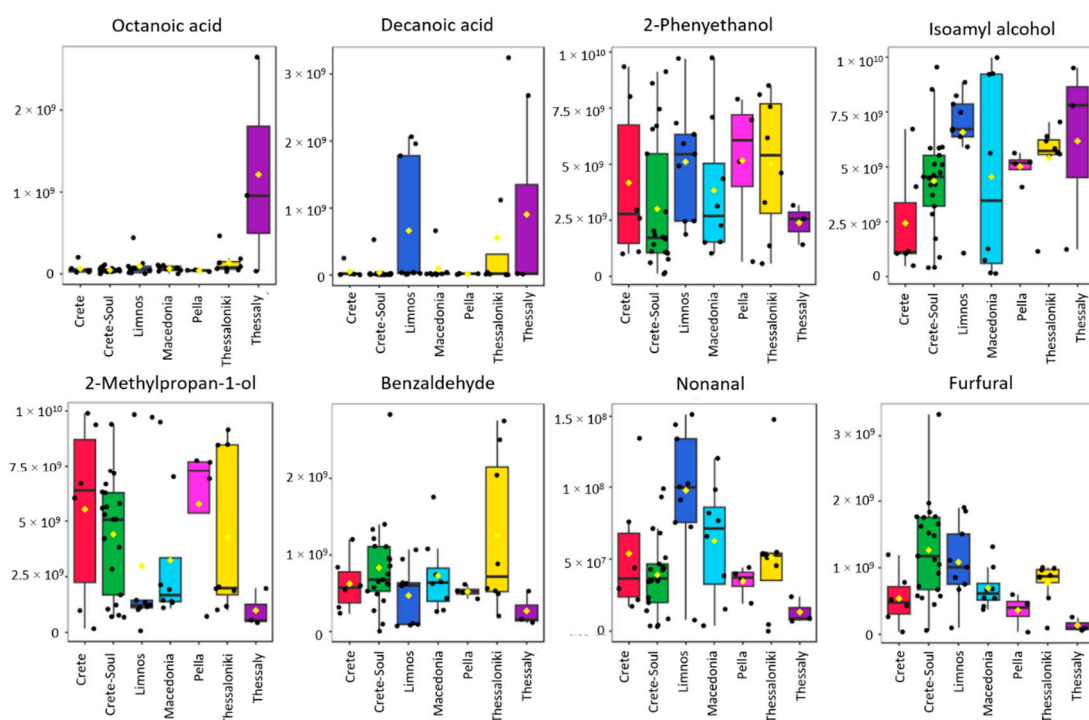


Figure S2. Boxplots of representative acids, alcohols and carbonyl compounds among Greek grape marc spirit samples. Black dots represent the samples' values and yellow dots are the mean values.

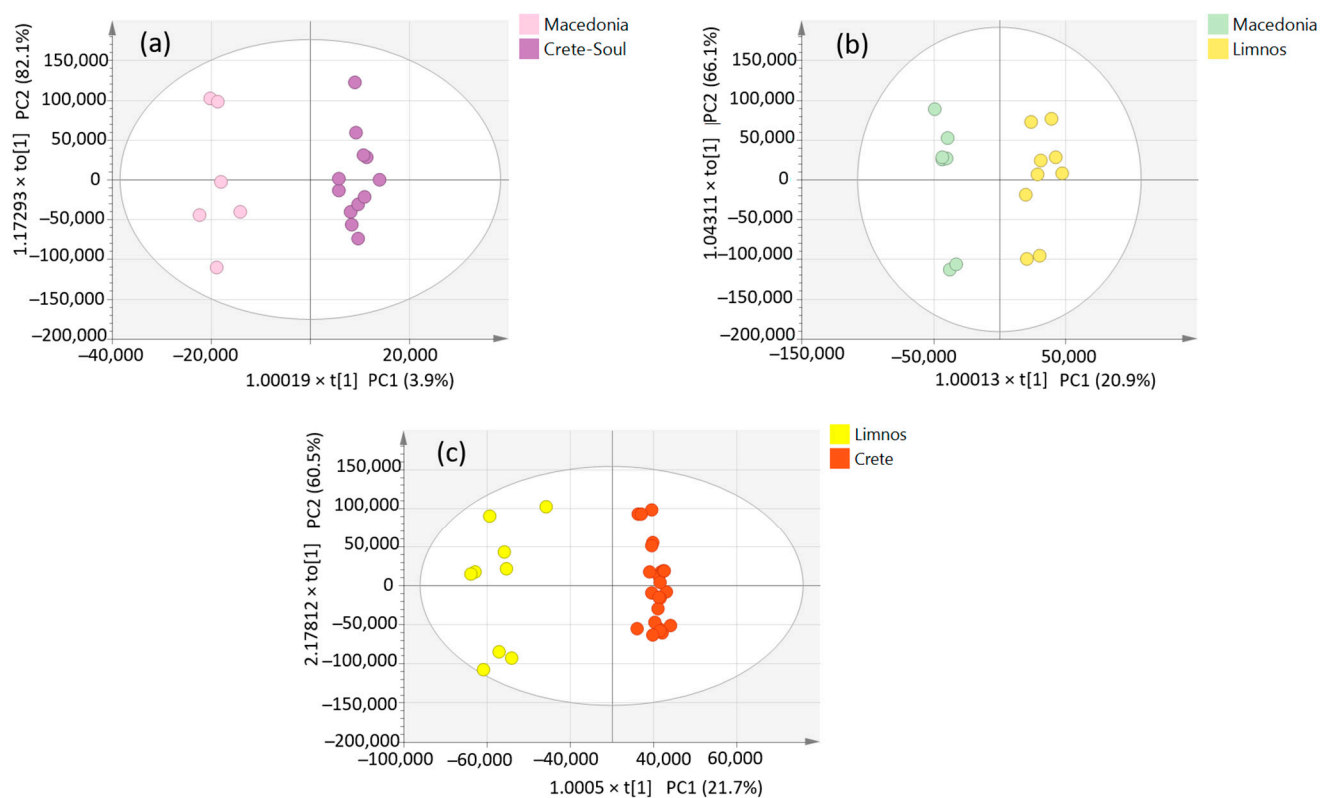


Figure S3. OPLS-DA score plots of the discrimination of (a) Macedonia and Crete-Soultanina, (b) Macedonia and Limnos and (c) Limnos and Crete grape marc spirit samples.

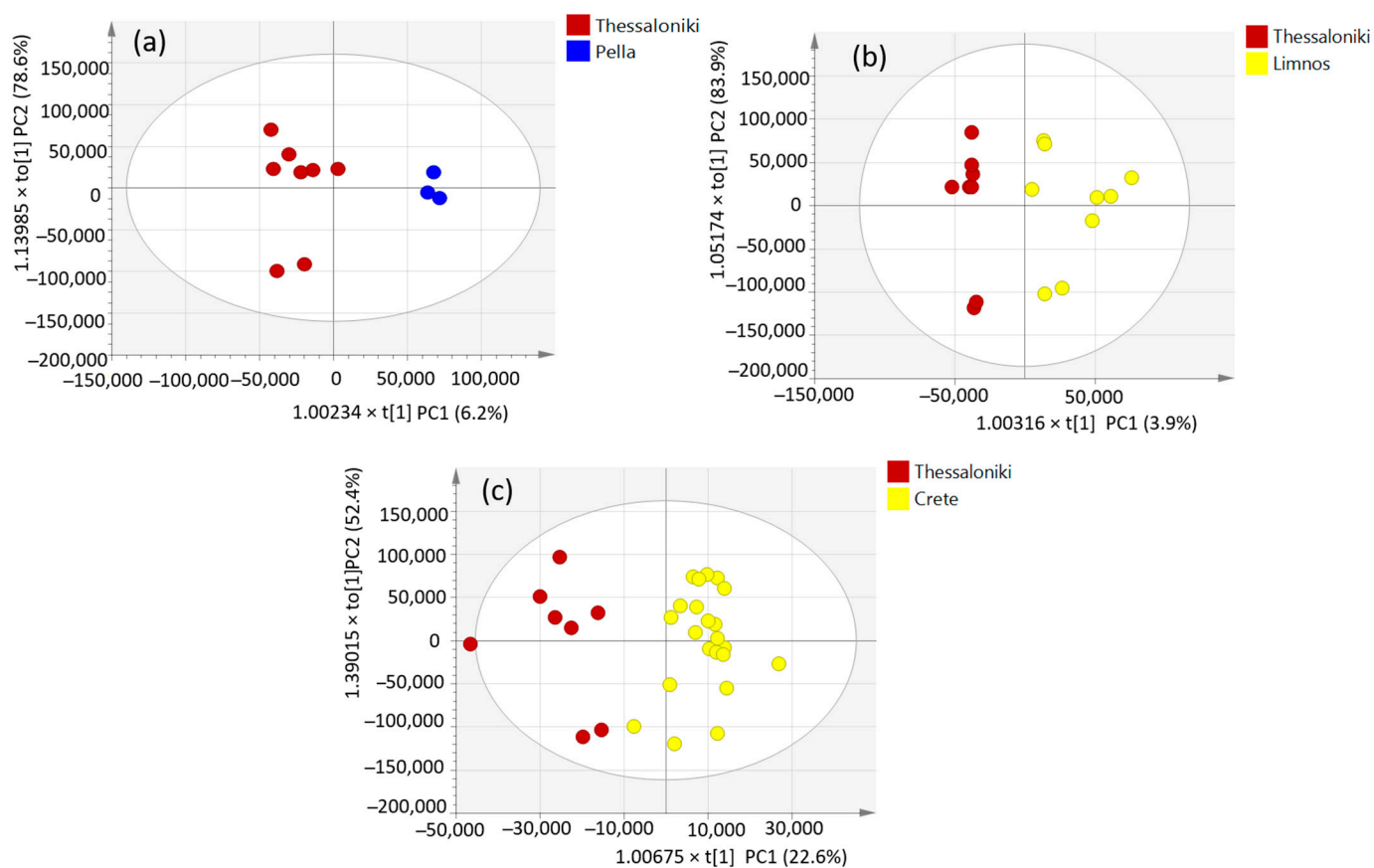


Figure S4. OPLS-DA score plots of the discrimination of (a) Thessaloniki and Pella, (b) Thessaloniki and Limnos and (c) Thessaloniki and Crete grape marc spirit samples.