Supplementary Materials.

Table S1. List of 54 compounds used for PCA analysis identified by the NIST 17 library from aged red wine. Identification quality > 70%.

Number	Compounds	Number	Compounds
1	2,3-Butanediol 1	28	3-hydroxydodecanoic acid
2	2,3-Butanediol 2	29	Oxaloacetic acid
3	1,3-Propanediol	30	Tyrosol
4	Lactic acid	31	2-Isopropylmalic acid
5	3-hydroxyisovaleric acid	32	Unknown 5
6	Unknown 1	33	1,2,3-ButaneTriol
7	Glyoxylic acid	34	4-hydroxybenzoic acid
8	2-Furoic acid	35	⌾-ketoglutaric acid
9	1,4-Butanediol	36	3,3-dimethyl glutaric acid
10	Pyruvic acid	37	Tartaric acid
11	4-hydroxybutanoic acid	38	Phloretic acid
12	2-hydroxyvaleric acid	39	Vanillic acid
13	Sorbic acid	40	2,6-dihydroxybenzoic acid
14	Glyoxime	41	Protocatechuic acid
15	2-Phenylethanol	42	Citric acid
16	1-Propanol	43	Isocitric acid
17	Hexanoic acid	44	Unknown 6
18	Unknown 2	45	Syringic acid
19	Methyl ethyl Succinic acid	46	4-hydroxy phenyllactic acid
20	Unknown 3	47	4-Coumaric acid
21	Octanoic acid	48	Ethyl Gallate
22	Glycerol	49	Shikimic acid
23	Succinic acid	50	Gallic acid
24	2-Pentanol	51	Palmitic acid
25	Unknown 4	52	Caffeic acid
26	Citramalic acid	53	4-Hydroxyphenyllactic acid
27	Malic acid	54	Stearic acid

Table S2. Characteristic ions and retention times of TMS derivatized organic acids, glycerol, **phenolic acids** and internal standard (tridecanoic acid) used for peak integration in SIM detection method according to [29] (Roessner et al., 2000).

Chromatogram number	Compounds	Retention time (min)	Characteristic ions (*m*/*z*)
1	Lactic acid	5.455	117, 133, 147, 191, 219, 234
2	Glyoxylic acid	7.141	73, 147, 190, 218, 233
3	Pyruvic acid	7.753	75, 95, 125, 151, 169, 184
4	Sorbic acid	8.186	73, 147, 214, 233, 261, 304
5	Glycerol	10.984	73, 103, 117, 133, 147, 205
6	Succinic acid	11.651	73, 129, 147, 247, 262
7	Fumaric acid	12.429	83, 133, 143, 147, 245
8	Citramalic acid	15.229	73, 115, 147, 247, 259, 349
9	Malic acid	15.724	73, 133, 147, 233, 245, 335
10	**Cinnamic acid**	**16.311**	**77, 103, 131, 161, 205, 220**
11	Oxaloacetic acid	16.452	73, 89, 142, 184, 276, 333
12	a-Ketoglutaric acid	18.411	73, 147, 156, 198, 229, 288
13	Tartaric acid	18.831	73, 147, 189, 219, 292, 423
14	Tridecanoic acid (IS)	20.288	73, 117, 129, 145, 271, 286
15	**Vanillic acid**	**20.636**	**73, 223, 267, 297, 312**
16	**Shikimic acid**	**21.823**	**73, 147, 204, 255, 372, 462**
17	Citric acid	21.944	147, 273, 347, 363, 375, 465
18	**Syringic acid**	**22.949**	**73, 253, 297, 312, 327, 342**
19	**p-Coumaric acid**	**23.484**	**73, 179, 219, 249, 293, 308**
20	**Gallic acid**	**24.098**	**73, 281, 355, 443, 458**
21	**Ferulic acid**	**25.870**	**73, 249, 293, 308, 323, 338**
22	**Caffeic acid**	**26.664**	**103, 147, 205, 292, 319, 333**

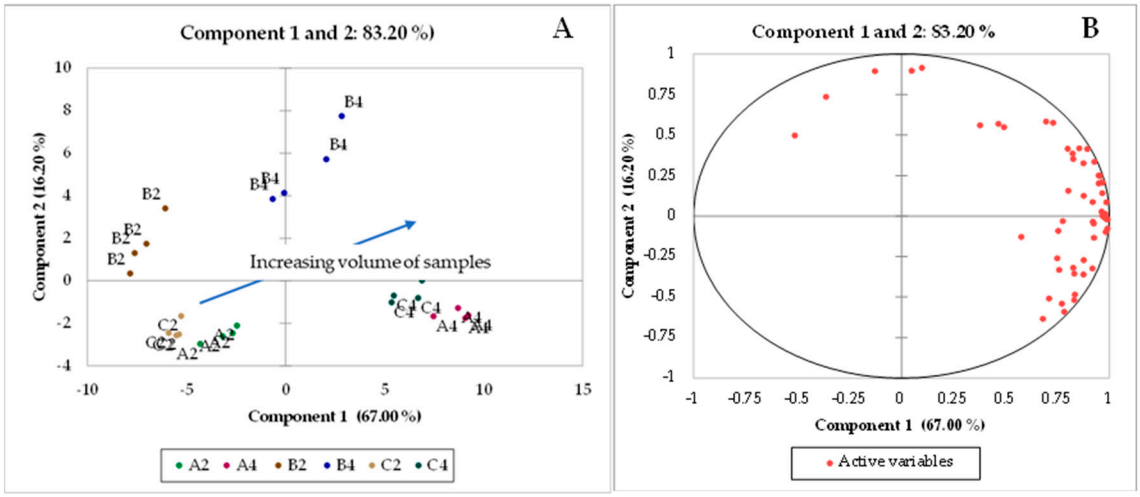

Figure S1. Graphs of the effect of extraction solvent on profiles of aged red wines obtained by hydroxylamine and MSTFA derivatization (A) and variable loadings (B). A, 2 x ethyl acetate; B, 1 x ethyl acetate + 1 x diethyl ether; C, 1 x ethyl acetate + 1 x MTBE. 2, 200 µl; 4,400 µl.

29 Roessner, U.; Wagner, C.; Kopka, J.; Trethewey, R.N.; Willmitzer, L. Simultaneous analysis of metabolites in potato tuber by gas chromatography-mass spectrometry. *Plant J.* **2000**, *23*, 131–142. https://doi.org/10.1046/j.1365-313x.2000.00774.x.