Discrimination of Smoke-Exposed Pinot Noir Wines by Volatile Phenols and Volatile Phenol-Glycosides

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Abbreviations

Volatile phenols (VPs)

Solid-phase microextraction and gas chromatography-mass spectrometry (SPME-GC-MS)

High-performance liquid chromatography combined with high-resolution accurate Tandem mass spectrometry (HPLC-HR-MS/MS)

Two-dimensional correlation spectroscopy (2D-COS)

Mid-infrared (MIR)

Isotope dilution assay (SIDA)

Australian Wine Research Institute's Commercial Services Laboratory (AWRI)

Stir bar sorptive extraction (SBSE)

Ultra high-performance liquid chromatography-quadrupole time-of-flight mass spectrometry (uHPLC-QToF)

Internal standards (IS)

Mass selective detector (MSD)

Selective ion monitoring (SIM)

Electrospray ionization (ESI)

Data-dependent acquisitions (DDAs)

Collision energy spread (CES)

Principal component analysis (PCA)

Partial least squares-discriminant analysis (PLS-DA)

Table S1. Standard curves for free and total volatile phenol analysis by HS-SPME-GC-MS

Compounds	*m/z*	Linear range (μg/L)	R^2		Equation	
			Free-form	Total	Free-form	Total
guaiacol-d_4 (IS)	113, 128					
guaiacol	124, 109	0.05-25	0.9999	0.9999	y=0.8874x+0.02406	y=0.9369x+0.0038
4-methylguaiacol-d_3 (IS)	141, 126					
4-methylguaiacol	138, 123	0.05-25	0.9998	0.9999	y=0.8885x+0.03685	y=0.9299x+0.0068
o-cresol-d_7 (IS)	115, 113					
o-cresol	108, 107	0.05-25	0.9997	0.9999	y=1.035x+0.02836	y=1.032x-0.00085
p-cresol-d_7 (IS)	115, 113					
p-cresol	108, 107	0.05-25	0.9996	0.9999	y=1.205x+0.06058	y=1.170x+0.0020
m-cresol-d_7 (IS)	115,113					
m-cresol	108, 107	0.05-25	0.9996	0.9997	y=1.428x+0.06449	y=1.454x+0.0015

IS: Internal Standard

Table S2. Targeted volatile phenols analysis by SPME-GC-MS.

			Total VPs (µg/L)				**Free VPs (µg/L)**				
Sample	**Group**	**guaiacol**	**4-methylguaiacol**	***o*-cresol**	***p*-cresol**	***m*-cresol**	**guaiacol**	**4-methylguaiacol**	***o*-cresol**	***p*-cresol**	***m*-cresol**
1	Non-smoke	18.0	1.8	4.4	8.5	1.0	7.5	0.9	1.8	2.1	0.8
2	Non-smoke	20.3	3.2	4.6	9.9	3.2	7.6	2.7	1.3	1.0	6.5
3	Non-smoke	17.8	2.2	4.4	9.8	1.080	6.6	1.6	2.2	2.4	2.2
4	Non-smoke	23.4	3.9	4.2	7.0	0.8	13.1	3.9	1.6	1.6	1.0
5	Non-smoke	22.0	2.4	4.2	8.8	0.9	10.5	2.2	2.4	1.9	3.5
6	Non-smoke	15.2	1.6	3.6	7.4	0.55	5.3	1.0	1.4	1.3	1.4
7	Non-smoke	18.7	1.8	3.4	8.2	0.6	7.2	1.3	1.4	1.1	1.6
8	Non-smoke	18.7	1.6	4.0	6.2	0.7	6.2	0.7	1.7	2.1	1.2
9	Non-smoke	19.0	3.6	3.8	9.1	1.1	8.3	3.8	0.6	1.3	0.5
10	Non-smoke	18.6	1.2	3.9	6.2	0.9	5.4	0.6	1.4	1.0	0.5
11	Non-smoke	16.5	2.0	3.8	9.3	1.0	4.3	1.1	1.4	1.9	0.5
12	Non-smoke	17.2	4.4	3.9	9.2	0.8	5.1	3.7	1.4	0.9	0.2
13	Non-smoke	14.4	1.2	3.6	6.8	0.5	4.4	0.5	1.4	0.9	0.7
14	Non-smoke	17.8	1.3	3.6	3.8	0.5	4.4	0.6	1.6	0.9	0.6
Mean	**Non-smoke**	**18.4**	**2.3**	**4.0**	**7.8**	**1.0**	**6.8**	**1.8**	**1.5**	**1.5**	**1.6**
15	Smoke	121.1	29.3	35.3	27.9	5.6	58.1	14.1	20.8	14.6	17.9
16	Smoke	130.8	32.6	36.0	36.9	6.4	60.3	16.2	16.8	18.1	18.4

17	Smoke	120.0	26.2	33.6	29.5	8.0	49.8	11.8	18.3	13.4	14.4
18	Smoke	189.6	48.4	46.6	35.8	10.5	88.2	20.4	27.1	15.8	27.4
19	Smoke	188.7	67.1	38.8	11.0	23.9	81.8	17.82	23.9	5.3	20.0
20	Smoke	381.2	215.4	85.5	61.5	23.9	183.5	51.2	40.9	7.2	39.0
21	Smoke	119.0	38.9	26.6	28.7	22.3	37.6	7.2	8.4	7.5	8.0
22	Smoke	115.8	35.2	31.6	27.6	20.4	39.2	10.2	14.4	7.6	11.8
23	Smoke	212.5	91.5	45.8	47.5	46. 5	105.6	37.2	27.5	7.7	28.4
24	Smoke	164.0	55.4	42.1	50.8	24.9	71.6	18.0	23.4	16.0	17.7
25	Smoke	316.0	116.6	56.0	50.9	49.7	191.9	53.0	40.2	23.5	37.9
26	Smoke	176.0	5.2	13.9	13.1	0.8	38.6	0.9	4.9	2.0	1.4
27	Smoke	13.2	1.8	5.2	7.4	1.3	4.0	1.0	3.3	1.1	1.3
28	Smoke	13.7	2.0	7.2	10.5	3.2	3.7	0.8	3.1	0.9	1.6
29	Smoke	12.6	2.2	5.3	8.4	1.2	4.0	0.9	2.8	1.5	1.461
30	Smoke	12.7	2.1	6.4	11.5	1.1	3.9	0.9	3.0	1.9	1.5
31	Smoke	12.7	1.9	5.2	7.9	1.2	2.9	0.7	2.4	1.0	1.0
32	Smoke	12.8	1.9	4.6	7.2	0.9	3.3	0.8	2.3	1.11	1.1
33	Smoke	13.7	2.0	5.2	6.1	1.4	4.2	1.0	3.0	0.8	1.4
34	Smoke	17.3	3.1	6.8	7.1	2.7	6.5	1.7	3.8	1.5	2.2
Mean	**Smoke**	**117.2**	**38.9**	**26.9**	**24.4**	**12.8**	**51.9**	**13.3**	**14.5**	**7.4**	**12.7**

Notes: Non-smoke, non-smoke-exposed**;** Smoke, smoke-exposed

Table S3. Thirty-five tentative annotated glycosides (level 2 annotations) identified from non-smoke-exposed and smoke-exposed wines.

No.	Accepted Compound ID[a]	Adducts detected	Formula	Exact mass	Mass Error (ppm)
1	Syringyl-β-D-Glucopyranoside-Iso	$[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$	$C_{14}H_{20}O_8$	316.1158	-3.14
2	Syringyl-β-D-Glucopyranoside	$[M+NH_4]^+$, $[M+Na]^+$	$C_{14}H_{20}O_8$	316.1158	-2.24
3	Deoxyhexose-H-Cresol	$[M+NH_4]^+$, $[M+Na]^+$	$C_{19}H_{28}O_{10}$	416.1682	-3.50
4	Deoxyhexose-H-Cresol-Iso	$[M+Na]^+$	$C_{19}H_{28}O_{10}$	416.1682	-3.69
5	Deoxyhexose-H-P-Phenol	$[M+Na]^+$	$C_{23}H_{34}O_{14}$	534.1948	-4.10
6	Deoxyhexose-P-4-Ethylguaiacol	$[M+Na]^+$	$C_{20}H_{30}O_{10}$	430.1839	-1.93
7	Guaiacyl-β-D-Gentiobioside-Iso1	$[M+NH_4]^+$	$C_{19}H_{28}O_{12}$	448.1581	-4.50
8	Guaiacyl-β-D-Gentiobioside	$[M+Na]^+$	$C_{19}H_{28}O_{12}$	448.1581	-4.12
9	Guaiacyl-β-D-Gentiobioside-Iso2	$[M+Na]^+$	$C_{19}H_{28}O_{12}$	448.1581	-4.11
10	Guaiacyl-β-D-Gentiobioside-Iso3	$[M+Na]^+$	$C_{19}H_{28}O_{12}$	448.1581	7.61
11	H-4-Methylguaiacol	$[M+NH_4]^+$	$C_{14}H_{20}O_7$	300.1209	-3.68
12	H-4-Methylguaiacol-Iso2	$[M+H]^+$	$C_{14}H_{20}O_7$	300.1209	-3.18
13	H-4-Methylsyringol	$[M+Na]^+$	$C_{15}H_{22}O_8$	330.1315	-1.53
14	H-Guaiacol	$[M+Na]^+$	$C_{13}H_{18}O_7$	286.1052	-2.00
15	H-Guaiacol-Iso2	$[M+Na]^+$	$C_{13}H_{18}O_7$	286.1052	-3.35
16	H-Guaiacol-Iso3	$[M+Na]^+$	$C_{13}H_{18}O_7$	286.1052	-3.56
17	H-H-P-4-Ethylguaiacol-Iso1	$[M+H-H_2O]^+$	$C_{24}H_{36}O_{14}$	548.2105	-7.46

18	H-H-P-4-Ethylguaiacol	$[M+H]^+$	$C_{24}H_{36}O_{14}$	548.2105	-7.68
19	H-H-P-4-Ethylguaiacol-Iso2	$[M+H-H_2O]^+$	$C_{24}H_{36}O_{14}$	548.2105	-9.13
20	Benzyl O-[arabinofuranosyl-(1->6)-glucoside]	$[M+NH_4]^+$	$C_{18}H_{26}O_{10}$	402.1526	-4.49
21	H-P-4-Methylguaiacol-Iso	$[M+Na]^+$	$C_{19}H_{28}O_{11}$	432.1632	-4.63
22	H-P-4-Methylguaiacol	$[M+H]^+$	$C_{19}H_{28}O_{11}$	432.1632	-7.97
23	H-P-Guaiacol	$[M+Na]^+$	$C_{18}H_{26}O_{11}$	418.1475	-7.79
24	H-P-Guaiacol-Iso1	$[M+Na]^+$	$C_{18}H_{26}O_{11}$	418.1475	-5.29
25	H-P-Guaiacol-Iso2	$[M+Na]^+$	$C_{18}H_{26}O_{11}$	418.1475	-3.63
26	H-P-Guaiacol-Iso3	$[M+Na]^+$	$C_{18}H_{26}O_{11}$	418.1475	-4.93
27	H-P-P-4-Methylguaiacol	$[M+Na]^+$	$C_{24}H_{36}O_{15}$	564.2054	-4.72
28	P-H-Cresol	$[M+H]^+$	$C_{18}H_{26}O_{10}$	402.1526	-6.84
29	P-H-Cresol-Iso2	$[M+H-H_2O]^+$	$C_{18}H_{26}O_{10}$	402.1526	-7.78
30	P-H-Cresol-Iso3	$[M+H-H_2O]^+$	$C_{18}H_{26}O_{10}$	402.1526	-9.25
31	P-H-Cresol-Iso4	$[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$	$C_{18}H_{26}O_{10}$	402.1526	-3.61
32	P-P-H-Cresol	$[M+Na]^+$	$C_{23}H_{34}O_{14}$	534.1948	-2.80
33	Syringyl-β-D-Gentiobioside	$[M+NH_4]^+$	$C_{20}H_{30}O_{13}$	478.1686	-4.53
34	Syringyl-β-D-Gentiobioside-Iso1	$[M+H]^+$, $[M+Na]^+$	$C_{20}H_{30}O_{13}$	478.1686	-8.89
35	Syringyl-β-D-Gentiobioside-Iso2	$[M+H-H_2O]^+$	$C_{20}H_{30}O_{13}$	478.1686	-8.01

[a] H-Hexose; P-Pentose; Iso-Isomer

Table S4. Correlation matrix for VPs and VP-glycosides in non-smoke-exposed and smoke-exposed wines with Pearson's correlation analysis.

	4-methylguaiacol-free	*p*-cresol-free	guaiacol-total	guaiacol-free	*m*-cresol-free	4-methylguaiacol-total	*p*-cresol-total	*m*-cresol-total	*o*-cresol-total	*o*-cresol-free
Syringyl-β-D-Glucopyranoside-Iso	0.15	0.18	0.17	0.11	0.28	0.26	0.29	0.39	0.36	0.38
H-Guaiacol-Iso2	0.15	0.23	0.26	0.17	0.25	0.28	0.34	0.35	0.39	0.39
P-H-Cresol-Iso2	0.16	0.18	0.23	0.15	0.29	0.28	0.32	0.38	0.39	0.38
H-4-Methylguaiacol-Iso2	0.19	0.23	0.25	0.19	0.38	0.30	0.32	0.41	0.42	0.46
H-P-4-Methylguaiacol-Iso	0.22	0.33	0.25	0.19	0.37	0.32	0.42	0.46	0.44	0.46
Syringyl-β-D-Gentiobioside-Iso2	0.14	0.22	0.28	0.21	0.28	0.25	0.32	0.25	0.36	0.36
Deoxyhexose-H-Cresol	0.20	0.26	0.32	0.24	0.31	0.34	0.36	0.45	0.43	0.42
Guaiacyl-β-D-Gentiobioside-Iso3	0.19	0.21	0.32	0.25	0.36	0.33	0.32	0.44	0.41	0.42
P-H-Cresol-Iso4	0.20	0.27	0.23	0.18	0.28	0.31	0.32	0.42	0.37	0.35
Deoxyhexose-P-4-Ethylguaiacol	0.34	0.29	0.29	0.26	0.38	0.44	0.40	0.54	0.50	0.53
H-H-P-4-Ethylguaiacol-Iso1	0.23	0.30	0.31	0.24	0.30	0.35	0.36	0.40	0.45	0.47
H-H-P-4-Ethylguaiacol	0.19	0.23	0.26	0.18	0.31	0.31	0.32	0.39	0.42	0.43

P-H-Cresol-Iso3	0.17	0.10	0.08	0.05	0.26	0.22	0.21	0.35	0.28	0.31
Syringyl-β-D-Gentiobioside-Iso1	0.11	0.19	0.15	0.10	0.28	0.21	0.26	0.29	0.35	0.39
H-4-Methylsyringol	0.17	0.09	0.24	0.17	0.27	0.27	0.22	0.31	0.35	0.35
H-Guaiacol	0.29	0.19	0.27	0.24	0.36	0.35	0.30	0.40	0.42	0.45
H-Guaiacol-Iso3	0.32	0.43	0.28	0.27	0.45	0.38	0.41	0.46	0.46	0.50
H-P-P-4-Methylguaiacol	0.28	0.36	0.26	0.23	0.39	0.33	0.40	0.41	0.39	0.38
Syringyl-β-D-Gentiobioside	0.28	0.31	0.24	0.22	0.42	0.34	0.31	0.44	0.42	0.45
Syringyl-β-D-Glucopyranoside	0.21	0.40	0.33	0.27	0.28	0.30	0.42	0.28	0.41	0.36
H-4-Methylguaiacol	0.19	0.27	0.29	0.23	0.24	0.32	0.31	0.41	0.41	0.39
H-H-P-4-Ethylguaiacol-Iso2	0.23	0.23	0.33	0.26	0.18	0.33	0.31	0.27	0.40	0.41
P-P-H-Cresol	0.40	0.31	0.41	0.38	0.36	0.43	0.39	0.43	0.47	0.48
H-P-Guaiacol	0.75	0.77	0.78	0.77	0.80	0.82	0.77	0.79	0.86	0.85
H-P-Guaiacol-Iso1	0.58	0.68	0.71	0.65	0.63	0.70	0.71	0.74	0.76	0.74
Deoxyhexose-H-Cresol-Iso	0.35	0.39	0.41	0.37	0.49	0.45	0.49	0.51	0.56	0.61
P-H-Cresol	0.41	0.38	0.41	0.36	0.49	0.49	0.49	0.57	0.56	0.59
Guaiacyl-β-D-Gentiobioside	0.37	0.35	0.31	0.32	0.48	0.41	0.44	0.51	0.47	0.53
H-P-4-Methylguaiacol	0.22	0.45	0.48	0.41	0.46	0.38	0.42	0.37	0.55	0.58
Guaiacyl-β-D-Gentiobioside-Iso1	0.42	0.58	0.57	0.54	0.52	0.51	0.52	0.45	0.58	0.61

H-P-Guaiacol-Iso3	0.33	0.23	0.10	0.17	0.26	0.21	0.27	0.22	0.20	0.26
Guaiacyl-β-D-Gentiobioside-Iso2	0.51	0.54	0.44	0.45	0.57	0.51	0.54	0.51	0.55	0.58
H-P-Guaiacol-Iso2	0.40	0.49	0.33	0.35	0.44	0.40	0.47	0.45	0.43	0.43
Deoxyhexose-H-P-Phenol	0.22	0.30	0.13	0.17	0.39	0.19	0.24	0.22	0.28	0.38
Benzyl O-[arabinofuranosyl-(1->6)-glucoside]	0.20	0.45	0.37	0.36	0.41	0.33	0.30	0.33	0.45	0.54

Table S5. Correlation matrix for VPs for non-smoke-exposed and smoke-exposed wines with Pearson's correlation analysis.

	4-Methylguaiacol -free	*p*-Cresol -free	Guaiacol -total	Guaiacol -free	*m*-Cresol -free	4-Methylguaiacol -total	*p*-Cresol -total	*m*-Cresol -total	*o*-Cresol -total	*o*-Cresol -free
4-Methylguaiacol -free		0.87	0.88	0.93	0.88	0.96	0.89	0.89	0.89	0.85
p-Cresol-free	0.87		0.88	0.90	0.88	0.89	0.91	0.82	0.91	0.89
Guaiacol-total	0.88	0.88		0.99	0.87	0.95	0.89	0.85	0.95	0.90
Guaiacol-free	0.93	0.90	0.99		0.89	0.96	0.89	0.86	0.94	0.90
m-Cresol-free	0.88	0.88	0.87	0.89		0.90	0.87	0.90	0.92	0.92
4-Methylguaiacol -total	0.96	0.89	0.95	0.96	0.90		0.92	0.94	0.97	0.93
p-Cresol-total	0.89	0.91	0.89	0.89	0.87	0.92		0.88	0.93	0.88
m-Cresol-total	0.89	0.82	0.85	0.86	0.90	0.94	0.88		0.92	0.90
o-Cresol-total	0.89	0.91	0.95	0.94	0.92	0.97	0.93	0.92		0.98
o-Cresol-free	0.85	0.89	0.90	0.90	0.92	0.93	0.88	0.90	0.98	

Table S6. Correlation matrix for VP-glycosides for non-smoke-exposed and smoke-exposed wines with Pearson's correlation analysis.