# SUPPLEMENTARY DATA

**Table S1.** Content of non-acylated anthocyanin monomers identified in the different wine samples and the mean value for the different zones. Data are means from three replicates ± standard deviation; nd = not detected. Different letters within columns represent statical differences according to one-way ANOVA and Tukey post-hoc comparison test with a significance level of $p \leq 0.05$. The Malvidin/Cyanidin ratio (Mv/Cy) is expressed as mean values calculated within each zone. For each zone, the mean value (± sd) of each compound is also reported.

| mg/L | Cyanidin 3-O-glucoside | | Delphinidin 3-O-glucoside | | Peonidin 3-O-glucoside | | Malvidin 3-O-glucoside | | Petunidin 3-O-glucoside | | Mv/Cy (average) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 0.39 ±0.03 | j | 1.25 ±0.02 | l | 0.43 ±0.03 | m | 5.09 ±0.45 | k | 0.68 ±0.08 | i | 14.00 |
| | 3.78 ±0.13 | f | 7.61 ±0.2 | hij | 6.52 ±0.31 | efg | 85.86 ±6.32 | cd | 9.01 ±1.43 | cde | |
| | 1.48 ±0.09 | i | 6.65 ±0.019 | ij | 3.23 ±0.15 | jk | 63.69 ±0.99 | fg | 7.49± 2.32 | efg | |
| | 10.03 ±0.32 | b | 17.07 ±0.67 | b | 17.07 ±0.13 | a | 156.18 ±5.65 | a | 17.90 ±0.99 | a | |
| | 13.66 ±0.23 | a | 14.07 ±0.55 | c | 14.34 ±0.23 | b | 100.18 ±7.13 | c | 13.14 ±1.06 | b | |
| north-west | 4.70 ±0.31 | ef | 8.19 ±0.09 | ghi | 4.14 ±0.31 | hij | 30.05 ±2.34 | i | 5.84 ±0.32 | fgh | 5.80 |
| | 3.79 ±0.12 | fg | 9.46 ±0.62 | fgh | 3.08 ±0.12 | jk | 30.35 ±2.66 | i | 6.53 ±0.56 | efgh | |
| | 2.83 ±0.05 | gh | 6.51 ±0.51 | j | 2.07 ±0.19 | kl | 16.76 ±1.98 | j | 4.21 ±0.16 | gh | |
| | 10.44 ±0.54 | b | 15.91 ±0.39 | b | 7.50 ±0.34 | def | 49.50 ±3.04 | h | 10.58 ±1.32 | cde | |
| | 14.00 ±0.32 | a | 23.40 ±0.42 | a | 11.99 ±0.57 | c | 80.89 ±4.06 | d | 16.06 ±1.47 | a | |
| south-west | 3.68 ±0.21 | fg | 7.03 ±0.28 | hij | 3.33 ±0.08 | jk | 27.07 ±1.43 | i | 5.52 ±0.54 | gh | 14.03 |
| | 1.10 ±0.09 | ij | 3.09 ±0.32 | k | 1.17 ±0.23 | lm | 15.23 ±1.65 | j | 3.04 ±0.34 | ghi | |
| | 1.35 ±0.08 | i | 3.66 ±0.54 | k | 11.83 ±0.43 | c | 11.59 ±1.54 | jk | 3.18 ±0.65 | hi | |
| | 6.01 ±0.43 | d | 12.61 ±0.45 | cd | 11.96 ±0.25 | c | 112.62 ±4.32 | b | 14.20 ±1.65 | b | |
| | 5.39 ±0.18 | ef | 10.32 ±0.98 | fgh | 8.99 ±0.18 | def | 79.54 ±3.65 | de | 10.94 ±0.76 | cde | |
| north-east | 2.70 ±0.32 | h | 8.06 ±0.87 | ghi | 3.56 ±0.21 | ij | 52.32 ±4.32 | h | 7.77 ±3.42 | def | 11.27 |
| | 5.25 ±0.29 | ef | 11.28 ±0.77 | de | 5.62 ±0.36 | gh | 58.70 ±4.45 | g | 9.79 ±3.51 | efg | |
| | 4.33 ±0.62 | f | 10.34 ±0.38 | ef | 4.87 ±0.64 | ghi | 60.19 ±3.06 | g | 9.09 ±2.14 | efgh | |
| | 7.81 ±0.43 | c | 13.02 ±0.65 | cd | 8.02 ±0.87 | def | 73.21 ±4.21 | ef | 11.23 ±0.45 | bc | |
| | 6.67 ±0.59 | c | 11.78 ±1.01 | cd | 6.81 ±0.99 | fg | 57.43 ±2.32 | gh | 9.82 ±0.76 | cde | |

**SUPPLEMENTARY DATA**
Alfieri, G., Riggi, R., Modesti, M., Annesi, B., Mencarelli, F., De Santis, D., & Bellincontro, A. A first characterisation and classification of Montalcino wines in relation to production areas: combination of destructive, non-destructive and chemometrics analyses. *OENO One, 60*(1). https://oeno-one.eu/article/view/9411

| | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | |
|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 5.86 ± 5.73 | a | 9.32 ± 6.28 | a | 8.31 ± 7.14 | a | 82.20 ±54.99 | b | 9.64 ± 6.43 | a |
| north-west | 7.15 ± 4.84 | a | 12.69 ± 6.96 | a | 5.75 ± 4.04 | a | 41.51 ± 24.91 | a | 8.64 ± 4.76 | a |
| south-west | 3.50 ± 2.25 | a | 7.34 ± 4.13 | a | 5.45 ± 4.76 | a | 49.21 ± 44.72 | a | 7.37 ± 4.97 | a |
| north-east | 5.35 ± 1.99 | a | 10.89 ± 1.85 | a | 5.77 ± 1.72 | a | 60.37 ± 7.76 | b | 9.53 ± 1.25 | a |

**Table S2.** Content of the quercetin monomers identified in the different wine samples. Data are means from three replicates ± standard deviation; nd = not detected. Different letters within columns represent statical differences according to one-way ANOVA and Tukey post-hoc comparison test with a significance level of $p \leq 0.05$. For each zone, the mean value (± sd) of each compound is also reported

| mg/L | Quercetin 3-O-glucoside | | Quercetin 3-O-rutinoside | | Quercetin | | Kampferol | | Quercitin 3-O-ramnoside | |
|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 10.97 ±1.16 | l | 2.83 ±0.25 | hi | 9.15 ±1.23 | k | *nd* | b | 0.51 ±0.05 | cdefg |
| | 11.86 ±0.97 | kl | 7.98 ±0.54 | bcd | 28.02 ±1.1 | efg | *nd* | b | 1.01 ±0.09 | a |
| | 6.17 ±1.04 | m | 1.96 ±0.15 | i | 30.75 ±0.98 | e | *nd* | b | 0.29 ±0.03 | gh |
| | 26.69 ± 0.86 | c | 8.61 ±0.45 | bc | 23.83 ±1.32 | h | *nd* | b | 0.9 6±0.09 | ab |
| | 26.54 ±1.4 | c | 6.94 ±0.67 | cde | 23.42 ±0.85 | hi | *nd* | b | 0.18 ±0.10 | gh |
| north-west | 24.36 ±0.95 | cd | 6.51 ±0.58 | def | 29.29 ±1.99 | efg | *nd* | b | 0.59 ±0.07 | cdefg |
| | 19.57 ±0.75 | efg | 5.27 ±0.34 | efg | 30.34 ±1.39 | e | *nd* | b | 0.32 ±0.05 | efgh |
| | 21.14 ±1.09 | def | 5.97 ±0.89 | efg | 27.57 ±1.4 | fgh | *nd* | b | 0.30 ±0.03 | fgh |
| | 30.94 ±0.8 | b | 9.62 ±0.77 | b | 38.37 ±1.42 | d | *nd* | b | 0.73 ±0.11 | abc |
| | 34.31 ±1.56 | a | 12.28 ±0.93 | a | 46.95 ±1.38 | abc | *nd* | b | 0.22 ±0.04 | h |
| south-west | 19.79 ±1.39 | ghi | 5.00 ±0.25 | efg | 17.01 ±1.95 | i | *nd* | b | 0.54 ±0.05 | cdef |
| | 16.05 ±1.25 | hij | 4.63 ±0.21 | gh | 17.14 ±1.54 | j | *nd* | b | 0.55 ±0.09 | cde |
| | 13.69 ±1.2 | jk | 4.92 ±0.43 | fgh | 25.66 ±1.34 | gh | *nd* | b | 0.08 ±0.05 | h |
| | 16.58 ±1.38 | ghi | 9.36 ±0.68 | b | 46.78 ±1.09 | bc | 2.22 ±0.28 | a | 0.18 ±0.03 | h |
| | 11.45 ±1.2 | kl | 4.65 ±0.56 | fgh | 27.11 ±1.19 | gh | *nd* | b | 0.34 ±0.12 | defgh |
| north-east | 16.19 ±1.37 | ij | 8.77 ±0.71 | bcd | 36.94 ±0.84 | d | *nd* | b | 0.60 ±0.16 | cd |
| | 19.15 ±1.27 | fgh | 8.95 ±0.54 | b | 50.65 ±1.26 | a | *nd* | b | 0.68 ±0.11 | cdef |
| | 16.95 ±0.99 | ghi | 5.05 ±0.39 | efg | 29.72 ±1.3 | ef | *nd* | b | 0.58 ±0.19 | c |
| | 25.65 ±0.99 | c | 8.09 ±0.87 | bcd | 50.04 ±1.06 | ab | *nd* | b | 0.12 ±0.05 | h |
| | 22.3 ±0.74 | def | 6.14 ±0.76 | efg | 46.17 ±1.41 | c | *nd* | b | 0.71 ±0.12 | bc |
| | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 16.44 ± 9.53 | a | 5.66 ± 3.05 | a | 23.03 ± 8.33 | a | 0.00 | a | 0.59 ±0.38 | a |
| north-west | 26.06 ± 6.34 | b | 7.93 ± 2.94 | a | 34.5 ± 8.1 | b | 0.00 | a | 0.43 ±0.21 | a |
| south-west | 15.51 ±3.14 | a | 5.7 ± 2.04 | a | 26.74 ±12.14 | a | 0.44 ± 0.99 | b | 0.33 ±0.21 | a |
| north-east | 20.04 ±3.93 | b | 7.39 ± 1.72 | a | 42.7 ± 9.09 | b | 0.00 | a | 0.54 ±0.23 | a |

**Table S3.** Content of flavanols identified in the different wine samples. Data are means from three replicates ± standard deviation; nd = not detected. Different letters within columns represent statical differences according to one-way ANOVA and Tukey post-hoc comparison test with a significance level of $p \leq 0.05$. For each zone, the mean value (± sd) of each compound is also reported.

| mg/L | Catechin | | (-)-Epicatechin | | Procyanidin B1 | | Procyanidin B2 | | Procyanidin B3 | | Procyanidin trimer C1 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 17.94 ±0.74 | k | 5.72 ±0.67 | i | 43.04 ±4.14 | ijk | 2.00 ±1.31 | e | 23.22 ±3.21 | j | 0.36 ±0.23 | bcd |
| | 77.13 ±3.02 | bcd | 34.84 ±4.44 | cde | 54.83 ±4.54 | efghi | 13.81 ±1.33 | cd | 37.63 ±1.65 | efgh | 1.13 ±0.23 | abc |
| | 41.85 ±3.43 | h | 19.02 ±4.78 | fgh | 71.16 ±4.17 | ab | 28.53 ±2.01 | b | 35.20 ±2.12 | efgh | 0.67 ±0.21 | bcd |
| | 71.48 ±3.65 | cde | 42.81 ±2.47 | abc | 44.24 ±5.13 | ghij | 10.83 ±1.11 | cd | 42.57 ±1.99 | efg | 0.37 ±0.09 | bcd |
| | 85.21 ±4.02 | ab | 38.28 ±5.64 | bcd | 55.14 ±7.17 | cdef | 14.64 ±1.09 | cd | 42.86 ±3.21 | efg | 1.10 ±0.81 | a |
| north-west | 24.97 ±3.81 | jk | 23.54 ±3.54 | efg | 44.79 ±3.59 | hij | 19.26 ±2.43 | c | 31.17 ±2.62 | ghij | 1.61 ±0.87 | a |
| | 34.76 ±3.21 | hij | 7.39 ±0.94 | hi | 35.39 ±2.12 | k | 2.63 ±0.32 | e | 45.94 ±4.78 | de | 0.56 ±0.34 | bcd |
| | 27.83 ±2.02 | ijk | 14.85 ±1.22 | ghi | 52.73 ±1.76 | efgh | 11.16 ±2.43 | d | 25.93 ±1.13 | ij | 0.29 ±0.13 | cd |
| | 66.26 ±4.52 | ef | 22.62 ±2.14 | fg | 57.71 ±2.01 | defg | 13.22 ±4.17 | cd | 62.88 ±4.19 | bc | 0.41 ±0.32 | cd |
| | 62.87 ±5.34 | ef | 20.69 ±2.32 | efg | 50.29 ±3.54 | fghi | 17.37 ±1.92 | cd | 77.08 ±5.09 | ab | 0.05 ±0.03 | d |
| south-west | 63.43 ±4.17 | ef | 14.77 ±1.05 | ghi | 68.75 ±2.54 | bc | 13.60 ±1.77 | cd | 27.87 ±2.04 | hij | 0.83 ±0.95 | abcd |
| | 43.08 ±3.59 | hi | 29.19 ±2.01 | def | 79.63 ±4.67 | a | 17.05 ±0.99 | c | 21.69 ±1.91 | j | 1.58 ±1.54 | a |
| | 76.11 ±3.02 | bcd | 41.37 ±4.95 | ab | 52.82 ±4.99 | efgh | 25.79 ±0.84 | b | 23.03 ±1.18 | j | 1.58 ±0.21 | a |
| | 52.41 ±6.17 | fg | 26.94 ±2.43 | def | 39.61 ±1.09 | jk | 14.22 ±1.21 | cd | 35.30 ±3.82 | fghi | 0.21 ±0.45 | bcd |
| | 80.97 ±3.97 | abc | 46.99 ±4.65 | a | 57.67 ±2.45 | defg | 25.30 ±2.32 | b | 33.67 ±3.98 | efghi | 1.2 ±0.13 | ab |
| north-east | 47.89 ±6.31 | gh | 19.59 ±2.31 | fg | 55.35 ±3.51 | defg | 10.89 ±1.29 | d | 39.25 ±4.08 | def | 0.2 ±0.42 | d |
| | 79.21 ±3.64 | abc | 23.77 ±2.14 | defg | 60.63 ±3.43 | cde | 27.24 ±2.41 | b | 68.59 ±4.75 | bc | 0.22 ±0.26 | d |
| | 70.01 ±6.43 | de | 22.39 ±3.54 | fg | 62.57 ±5.09 | cde | 27.60 ±3.09 | b | 56.40 ±4.98 | cd | 0.35 ±0.06 | bcd |
| | 85.13 ±8.41 | a | 27.56 ±2.43 | def | 83.87 ±4.68 | a | 32.15 ±4.98 | a | 55.02 ±4.23 | cd | 0.37 ±0.09 | cd |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 83.59 ±7.77 | ab | 22.46 ±1.43 | efg | 65.16 ±2.56 | bcd | 12.58 ±1.10 | cd | 79.92 ±6.17 | a | 0.22 ±0.14 | cd |
| | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | |
| south-east | 58.72 ± 28.06 | a | 28.13 ± 15.4 | a | 53.68 ± 11.3 | a | 13.96 ± 9.56 | a | 36.29 ± 8.0 | a | 0.72 ± 0.37 | a |
| north-west | 43.33 ± 19.73 | a | 17.81 ± 6.73 | b | 48.18 ± 8.52 | a | 12.72 ± 6.49 | a | 48.59 ± 21.44 | b | 0.58 ± 0.6 | a |
| south-west | 63.19 ± 15.84 | b | 31.85 ± 12.67 | a | 59.69 ± 15.28 | a | 19.19 ± 5.94 | a | 28.31 ± 6.11 | a | 1.08 ± 0.57 | a |
| north-east | 73.16 ± 15.3 | b | 23.15 ± 2.89 | a | 65.51 ± 10.87 | a | 22.09 ± 9.66 | a | 59.83 ± 15.32 | b | 0.27 ± 0.08 | a |

**Table S4.** Content of the phenolic acids identified in the different wine samples. Data are means from three replicates ± standard deviation; nd = not detected. Different letters within columns represent statical differences according to one-way ANOVA and Tukey post-hoc comparison test with a significance level of $p \leq 0.05$. For each zone, the mean value (± sd) of each compound is also reported.

| mg/L | Protocatechuic acid | | Gallic acid ethyl ester | | Gallic acid | | Caffeoyl tartaric acid | | P Coumaric acid | | Caffeic acid | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| south-east | 3.62 ±0.62 | ab | 20.18 ±1.43 | hij | 90.16 ±4.54 | cd | 0.38 ±0.37 | b | 0.10 ±0.06 | d | 14.09 ±1.04 | efg |
| | 0.49 ±0.25 | fg | 13.14 ±1.78 | j | 67.59 ±3.65 | ef | *nd* | b | 0.46 ±0.21 | d | 15.60 ±1.32 | def |
| | 0.58 ±0.31 | fg | 18.15 ±2.32 | hij | 87.64 ±6.43 | cd | *nd* | b | 0.09 ±0.32 | d | 16.40 ±0.99 | def |
| | 0.41 ±0.22 | fg | 12.39 ±0.45 | j | 48.05 ±4.12 | gh | *nd* | b | 0.20 ±0.11 | d | 11.72 ±1.54 | gh |
| | 1.66 ±0.55 | def | 15.73 ±1.13 | ij | 63.39 ±4.78 | fg | *nd* | b | 3.07 ±0.36 | ab | 19.09 ±1.32 | bc |
| north-west | 3.29 ±0.42 | bcd | 29.52 ±2.09 | cdef | 77.16 ±5.15 | def | 0.55 ±0.21 | b | 0.83 ±0.32 | d | 19.11 ±1.24 | bc |
| | 0.68 ±0.12 | fg | 26.69 ±2.54 | fgh | 78.47 ±6.44 | def | 1.28 ±0.15 | a | 1.01 ±0.16 | d | 28.42 ±4.21 | a |
| | 2.20 ±0.29 | cde | 41.91 ±6.98 | ab | 107.28 ±4.54 | a | 0.68 ±0.31 | a | 0.75 ±0.09 | d | 19.06 ±2.43 | bc |
| | 0.91 ±0.31 | efg | 39.04 ±1.65 | abc | 106.82 ±8.32 | ab | 0.20 ±0.11 | b | 0.59 ±0.09 | d | 18.99 ±1.76 | bc |
| | 0.70 ±0.76 | g | 44.13 ±2.14 | a | 107.11 ±7.65 | ab | *nd* | b | 2.43 ±0.19 | abc | 25.36 ±2.42 | a |
| south-west | 3.28 ±0.37 | bcd | 26.22 ±0.99 | efgh | 81.17 ±3.43 | cde | *nd* | b | 1.35 ±0.18 | cd | 23.02 ±2.87 | abc |
| | 4.94 ±0.48 | a | 29.41 ±1.91 | cdef | 88.45 ±2.13 | cd | 0.15 ±0.09 | b | 0.57 ±0.06 | d | 18.19 ±1.69 | cde |
| | 1.05 ±0.12 | efg | 26.21 ±2.31 | fgh | 71.07 ±2.43 | ef | *nd* | b | 0.58 ±0.08 | d | 13.67 ±1.21 | fgh |
| | 1.00 ±0.09 | efg | 19.84 ±3.13 | ghi | 39.72 ±1.65 | h | *nd* | b | 1.53 ±0.87 | bcd | 22.16 ±1.98 | a |
| | 0.91 ±0.49 | efg | 32.74 ±1.23 | bcd | 65.96 ± 3.23 | fg | 1.16 ±0.19 | a | 2.82 ±0.98 | a | 10.26 ±1.43 | h |
| north-east | 2.75 ±0.31 | bcd | 22.04 ±1.67 | ghi | 52.45 ±2.68 | gh | *nd* | b | 2.28 ±0.65 | ab | 22.25 ±2.22 | abc |
| | 3.27 ±0.61 | bcd | 30.43 ±3.07 | cdef | 64.92 ±4.21 | fg | *nd* | b | 3.97 ±0.89 | a | 24.56 ±2.12 | a |
| | 3.60 ±0.78 | ab | 28.78 ±2.54 | def | 77.29 ±7.43 | cdef | 0.18 ±0.17 | b | 2.96 ±0.65 | abc | 19.47 ±1.32 | bcd |
| | 4.02 ±0.83 | ab | 32.15 ±1.65 | cdef | 86.57 ±8.12 | bc | *nd* | b | 1.64 ±0.16 | bcd | 25.46 ±2.16 | a |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3.25 ±0.57 | bc | 29.14 ±2.56 | def | 69.92 ±2.07 | ef | 0.25 ±0.19 | b | 1.54 ±0.08 | bcd | 24.33 ±1.96 | a |
| | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | | Mean per area | |
| south-east | 1.35 ± 1.36 | a | 15.91 ± 3.29 | a | 71.36 ± 17.6 | a | 0.07 ± 0.16 | a | 0.78 ± 1.28 | a | 17.46 ± 5.47 | a |
| north-west | 1.55 ± 1.15 | a | 36.25 ± 7.72 | b | 95.36 ± 16.03 | a | 0.54 ± 0.49 | a | 1.12 ± 0.74 | a | 22.18 ± 4.42 | a |
| south-west | 2.23 ± 1.8 | a | 26.88 ± 4.77 | c | 69.27 ± 18.68 | b | 0.26 ± 0.5 | a | 1.37 ± 0.92 | a | 15.38 ± 2.73 | a |
| north-east | 3.37 ± 0.46 | b | 28.5 ± 3.84 | c | 70.23 ± 12.85 | b | 0.08 ± 0.11 | a | 2.47 ± 1.01 | b | 23.21 ± 2.4 | a |

**Table S5.** Content of the non-flavonoid stilbenes identified in the different wine samples. Data are means from three replicates ± standard deviation; nd = not detected. Different letters within columns represent statical differences according to one-way ANOVA and Tukey post-hoc comparison test with a significance level of $p \leq 0.05$. For each zone, the mean value (± sd) of each compound is also reported.

| mg/L | T-Resveratrol 3-O-glucoside | | Piceatannol | | (+)-Epsilon Viniferin | | Resveratrol | |
|---|---|---|---|---|---|---|---|---|
| south-east | 0.36 ±0.08 | d | 0.51 ±0.11 | cd | *nd* | d | *nd* | e |
| | 0.43 ±0.09 | d | 1.43 ±0.31 | a | *nd* | d | 0.78 ±0.07 | bc |
| | *nd* | d | 0.51 ±0.16 | bcd | *nd* | d | 0.31 ±0.13 | cde |
| | 0.30 ±0.23 | d | 1.40 ±0.23 | a | *nd* | d | 0.63 ±0.21 | bcd |
| | 2.54 ±0.29 | b | *nd* | d | *nd* | d | 0.30 ±0.12 | cde |
| north-west | 0.48 ±0.32 | d | *nd* | d | *nd* | d | 0.61 ±0.45 | bc |
| | 2.50 ±0.52 | b | *nd* | d | *nd* | d | 1.20 ±0.67 | b |
| | 1.42 ±0.24 | c | *nd* | d | *nd* | d | 0.55 ±0.24 | bcd |
| | 2.01 ±0.42 | b | *nd* | d | *nd* | d | 0.84 ±0.18 | bcd |
| | 4.28 ±0.28 | a | *nd* | d | *nd* | d | 2.12 ±0.55 | a |
| south-west | *nd* | d | *nd* | d | *nd* | d | 0.10 ±0.14 | e |
| | *nd* | d | *nd* | d | *nd* | d | *nd* | e |
| | *nd* | d | *nd* | d | *nd* | d | 1.04 ±0.65 | bc |
| | 0.18 ±0.10 | d | 1.23 ±0.32 | ab | *nd* | d | 1.13 ±0.21 | bc |
| | 2.12 ±0.21 | b | 1.10 ±0.52 | b | *nd* | d | 2.36 ±0.43 | a |
| north-east | 0.27 ±0.08 | d | 0.95 ±0.68 | b | 1.22 ±0.09 | bc | 0.88 ±0.09 | bcd |
| | *nd* | d | *nd* | d | 1.52 ±0.11 | a | 0.59 ±0.08 | bcd |
| | *nd* | d | 0.59 ±0.43 | d | 1.39 ±0.08 | b | 0.48 ±0.13 | bcd |
| | *nd* | d | *nd* | d | 1.61 ±0.21 | a | 0.52 ±0.15 | bcd |
| | *nd* | d | *nd* | d | 1.19 ±0.17 | bc | 0.49 ±0.19 | bcd |
| | Mean per area | | Mean per area | | Mean per area | | Mean per area | |
| south-east | 0.72 ± 1.02 | a | 0.76 ± 0.62 | a | 0.0 ± 0.0 | a | 0.4 ± 0.3 | a |
| north-west | 2.13 ± 1.41 | b | 0.0 ± 0.0 | b | 0.0 ± 0.0 | a | 1.06 ± 0.64 | a |
| south-west | 0.45 ± 0.93 | a | 0.46 ± 0.63 | a | 0.0 ± 0.0 | a | 0.92 ± 0.95 | a |
| north-east | 0.06 ± 0.13 | a | 0.3 ± 0.44 | a | 38.43 ± 0.02 | b | 0.59 ± 0.16 | a |

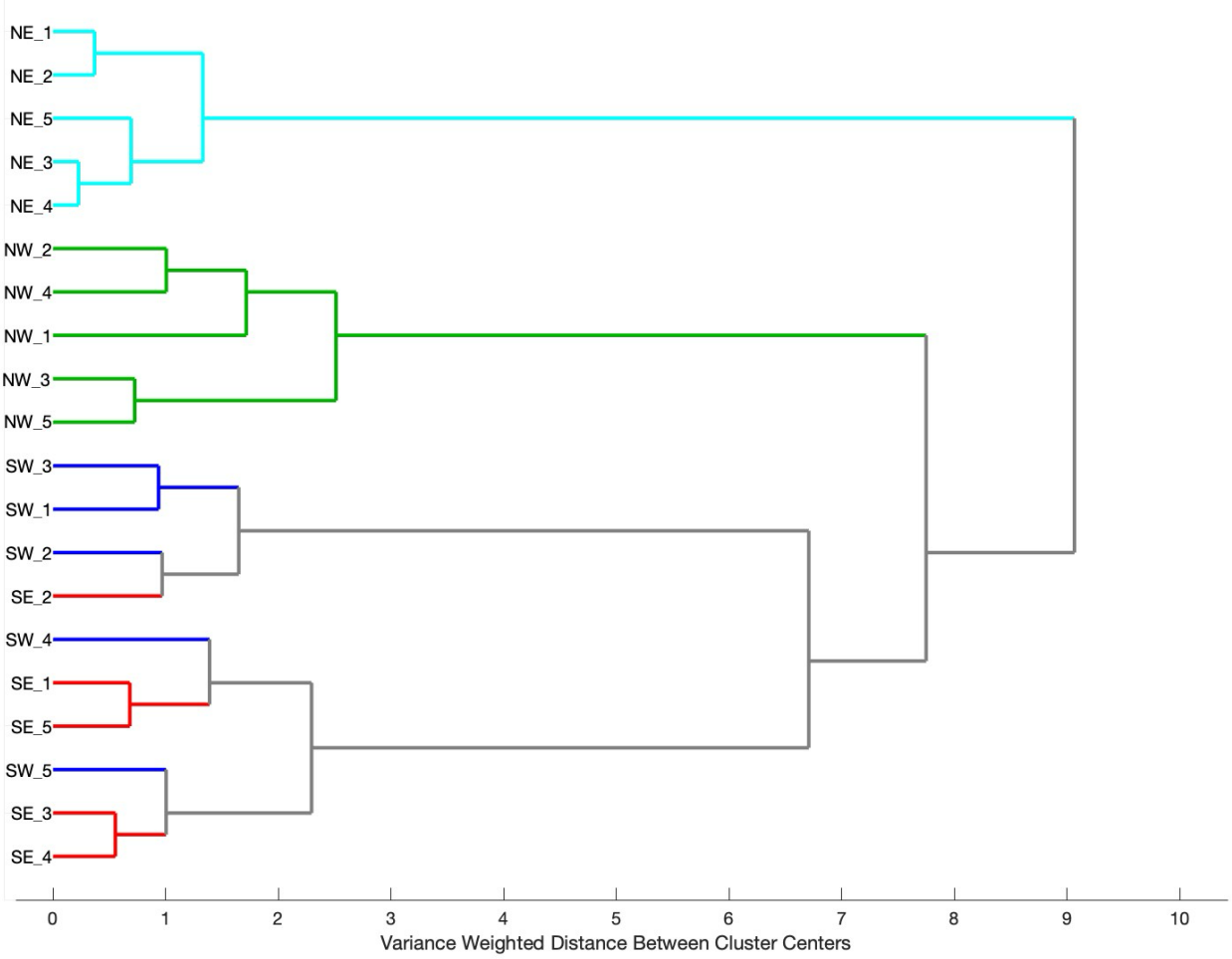



**Figure S1.** Two-way dendrogram obtained from the cluster analysis (by the Ward's method) performed on the polyphenols HPLC-DAD detected after their autoscaling pre-treatment. Wine production areas: south east (SE), north west (NW), south west (SW) and north east (NE).

**Table S6.** Confusion matrix of the PLS-DA model shown in figure 4. Err, total error; FNR, false negative ratio; FPR, false positive ratio; F1, F1-score; N, number of classes; P, precision = total positive (TP)/total positive + false positive; TNR, true negative ratio; TPR, true positive ratio.

| Confusion Matrix (Calibration) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Class | FRP | TNR | FNR | N | Err | P | F1 |
| SE (south east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| NW (north west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| SW (south west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| NE (north east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |

| Class | SE (south east) | NW (north west) | SW (south west) | NE (north east) |
|---|---|---|---|---|
| SE (south east) | 5 | 0 | 0 | 0 |
| NW (north west) | 0 | 5 | 0 | 0 |
| SW (south west) | 0 | 0 | 5 | 0 |
| NE (north east) | 0 | 0 | 0 | 5 |

| Matthew's Correlation Coefficient = 1.00 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Confusion Matrix (Cross Validation) | | | | | | | |
| Class | FRP | TNR | FNR | N | Err | P | F1 |
| SE (south east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| NW (north west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| SW (south west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| NE (north east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |

| class | SE (south east) | NW (north west) | SW (south west) | NE (north east) |
|---|---|---|---|---|
| SE (south east) | 5 | 0 | 0 | 0 |
| NW (north west) | 0 | 5 | 0 | 0 |
| SW (south west) | 0 | 0 | 5 | 0 |
| NE (north east) | 0 | 0 | 0 | 5 |
| Matthew's Correlation Coefficient = 1.00 | | | | |

**Table S7.** Volatile identified with HS GC-MS approach in wines and related retention time (RT).

| Aromatic Class | Compound | RT (min) |
|---|---|---|
| Alcohols | Ethyl alcohol (Ethanol) | 5.02 |
| | Phenylethyl alcohol | 16.04 |
| | 1-Hexanol | 12.72 |
| | 2-Hexenol | 13.24 |
| | 3-Hexen-1-ol | 15.05 |
| | 2-Hexen-1-ol, (E)- | 11.03 |
| | 1-Octen-3-ol | 16.98 |
| | 1-Octanol | 14.26 |
| | 2-Penten-1-ol, (Z)- | 10.02 |
| | Isopentyl alcohol | 10.65 |
| | 2-Propanol, 2-methyl- | 6.02 |
| | Isotridecyl alcohol | 20.09 |
| Aldehydes | Pentanal, 3-methyl- | 8.05 |
| | 3-Hexenal, (Z) | 9.32 |
| | 2-Heptanal, (Z) | 11.26 |
| | Nonanal | 12.95 |
| | 2,4-Hexadienal, (E,E)-A | 13.24 |
| | Decenal | 12.01 |
| | Butanal, 2-methyl- | 6.02 |
| | Butanal, 3-methyl- | 7.06 |
| | Benzeneacetaldehyde | 17.85 |
| Esters | Ethyl heptanoate | 18.36 |
| | Ethyl octanoate | 14.37 |
| | Ethyl acetate | 4.11 |
| | Ethyl caproate | 19.68 |
| | Ethyl caprylate | 18.32 |

| | | |
|---|---|---|
| | Ethyl caprate | 19.22 |
| | Diethyl succinate | 18.35 |
| | 3-Hexen-1-ol, acetate, (Z)- | 14.76 |
| Acids | Acetic acid | 7.08 |
| | Hexanoic acid | 19.08 |
| | Octanoic acid | 14.33 |
| | Butanoic acid | 22.65 |
| | Propanoic acid, 2,2 dimethyl | 21.35 |
| | Butanedioic acid | 20.98 |
| | Undecanoic acid | 22.56 |
| Ketones | 2-Nonenal, (E)- | 11.04 |
| | 2,3-Butanedione | 10.33 |
| | 5-Hexen-2-one | 9.85 |
| | 1-Heptyn-6-one | 24.25 |
| | 2-Heptanone, 4-methyl | 29.65 |
| Terpenoids | Linalool | 19.08 |
| | Calamenene | 18.66 |
| | Farnesene | 19.87 |
| | Cadinene | 21.05 |
| Lactones | Butyrolactone | 11.66 |
| Others | 1-Pentene | 7.03 |
| | Oxalic acid | 11.22 |
| | 3,3,5-Trimethylheptane | 16.66 |
| | 2,6-Dimethylnonane | 18.99 |
| | 4,6-Dimethyldodecane | 26.33 |
| | n-Nonadecane | 27.05 |
| | Hexadecane | 24.05 |

**Table S8.** Confusion matrix of the PLS-DA model shown in fig 8 in calibration prediction in which E-nose information was used as the dependent variable (x-block) and wines as the independent variable. Err, total error; FNR, false negative ratio; FPR, false positive ratio; F1, F1-score; N, number of classes; P, precision = total positive (TP)/total positive + false positive; TNR, true negative ratio; TPR, true positive ratio.

| PLSDA Classification Using Rule: Pred Most Probable | | | | | | | |
|---|---|---|---|---|---|---|---|
| Class | FRP | TNR | FNR | N | Err | P | F1 |
| Area 1 (south east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| Area 2 (north west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| Area 3 (south west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| Area 4 (north east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |

| class | Area 1 (south east) | Area 2 (north west) | Area 3 (south west) | Area 4 (north east) |
|---|---|---|---|---|
| Area 1 (south east) | 5 | 0 | 0 | 0 |
| Area 2 (north west) | 0 | 5 | 0 | 0 |
| Area 3 (south west) | 0 | 0 | 5 | 0 |
| Area 4 (north east) | 0 | 0 | 0 | 5 |

Matthew's Correlation Coefficient = 1.00

Confusion Matrix (CV) RESULTS

| Class | FRP | TNR | FNR | N | Err | P | F1 |
|---|---|---|---|---|---|---|---|
| Area 1 (south east) | 0.00 | 0.2 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| Area 2 (north west) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |
| Area 3 (south west) | 0.06667 | 0.93333 | 0 | 5 | 0.0500 | 0.83333 | 0.90909 |
| Area 4 (north east) | 0.00 | 1.00 | 0 | 5 | 0.00 | 1.00 | 1.00 |

| class | Area 1 (south east) | Area 2 (north west) | Area 3 (south west) | Area 4 (north east) |
|---|---|---|---|---|
| Area 1 (south east) | 4 | 0 | 0 | 0 |
| Area 2 (north west) | 0 | 5 | 0 | 0 |
| Area 3 (south west) | 1 | 0 | 5 | 0 |
| Area 4 (north east) | 0 | 0 | 0 | 5 |
| Matthew's Correlation Coefficient = 1.00 | | | | |