Supporting Information

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SI Text

Barrel Elaboration. After 13 months of natural drying, some of the staves were selected for assembling. Forty-eight barrels (12 lots times 4 repeats) were assembled and subsequently medium toasted for 45 min. These barrels were used for wine-aging experiments with the red Pinot noir wine from Mercurey and the white Chardonnay wine from Beaune. The remaining staves were further dried for an additional 43 months (giving a total drying duration of 56 months). Forty-eight new barrels were then assembled following the same procedure as before for wine-aging experiments with a red Syrah wine from Côte Rotie (Côtes du Rhône north) and a red Grenache wine from Gigondas (Côtes du Rhône south).

Wine Elaboration. For the first set of experiments (1998 harvest): at the end of the wine-aging period (11 months for the red, and 13 months for the white), bottling was realized after blending of the 2 repeats for each lot, thus providing us with 12 bottles of Mercurey and 12 bottles of Beaune. For the second set of experiments (2002 harvest): for the Côte Rotie wine, bottling was realized after 12 months of oak aging but separately for the 2 repeats. Therefore, we had at our disposal 2 sets of 12 bottles. For the Gigondas wine, bottling was realized after 6 months of oak aging and after blending of the 2 repeats.

Grape Seed and Skin Extracts and Flesh. After careful separation of the skin and seeds of fresh Pinot noir berries, extracts were obtained by intimately mixing 1 ml of pure methanol (LC-MS grade) with skins or seeds in a mortar, followed by an ultrasonic bath for 5 min. Each of these mixtures was then centrifuged (10 min, 25,400 $\times$ *g*). Next, 50 μl of supernatant was diluted in 1 ml of methanol before injection. The mesocarp sample was obtained by crushing the flesh of these berries in a mortar, followed by a dilution in methanol. Of this, 50 μl of eluted solution was diluted in 1 ml of methanol before injection.

Yeast Fermentation Medium. A synthetic fermentation medium with *Saccharomyces cerevisiae* cells was prepared with the following composition for 1 liter and pH 3.5: 120 g glucose, 120 g fructose, 2 g tartaric acid, 10 g D,L malic acid, 0.5 g NH_4Cl, 0.6 g Yeast Carbon Base and water. When the total sugar concentration reached a concentration lower than 2 g/l, indicating the end of the fermentation process, the hydroalcoholic medium was centrifuged (5 min, 10,000 $\times$ *g*) and the supernatant recovered. Of this supernatant, 20 μl was diluted in 1 ml of methanol before injection.

Tartar Precipitate. Red tartar "diamonds" were recovered from the bottom of the Vosne Romanée bottle and immediately soaked in water/methanol (50/50, vol/vol) for 30 min in an ultrasonic bath. After centrifugation (5 min, 10,000 $\times$ *g*), 100 μl of the supernatant were diluted in 1 ml of methanol before injection.

Oak Wood Extracts. Methanol extracts were obtained by soaking around 500 mg of untoasted, medium toasted (around 120 °C, 10 min), and heavy toasted (around 200 °C, 10 min) oak wood shavings (blend of sessile and pedunculate species) in 5 ml of methanol for 30 min in an ultrasonic bath. After centrifugation (5 min, 25,400 $\times$ *g*), 20 μl of the supernatant was diluted in 1 ml of methanol before injection.

Statistical Treatment. The primary advantage of using targeted profiling as an input to PLS-DA is generating variables that represent combinations of measured metabolite concentrations. Positive-regression coefficients indicate a relatively greater concentration of the considered metabolites with respect to the others, whereas negative values indicate a relatively lower concentration with respect to the other samples-classes. As such, these variables are easier to interpret as factors in the underlying classification model. Thus, targeted profiling provides meaningful and interpretable factors describing the input data.

The feature selection procedure comprises 2 steps: (*i*) identification of those masses that best describe each classes (a list based on the modeling power of the original variables) and (*ii*) scoring and ranking of the variables in every class-related list according to their abilities to discriminate the class they model from all other categories. The ranking and score take place after computation of the minimum number of masses through the formula generator (in-house code written in FORTRAN). The generated formulas were validated by setting sensible chemical constraints (N rule, O/C ratio $\leq$1, H/C ratio $\leq$ 2n + 2, element counts: C $\leq$100, O $\leq$80, $n \leq 5$, S $\leq$ 1) and only the masses in conjunction with their generated theoretical ^{13}C-isotope patterns were taken into consideration.

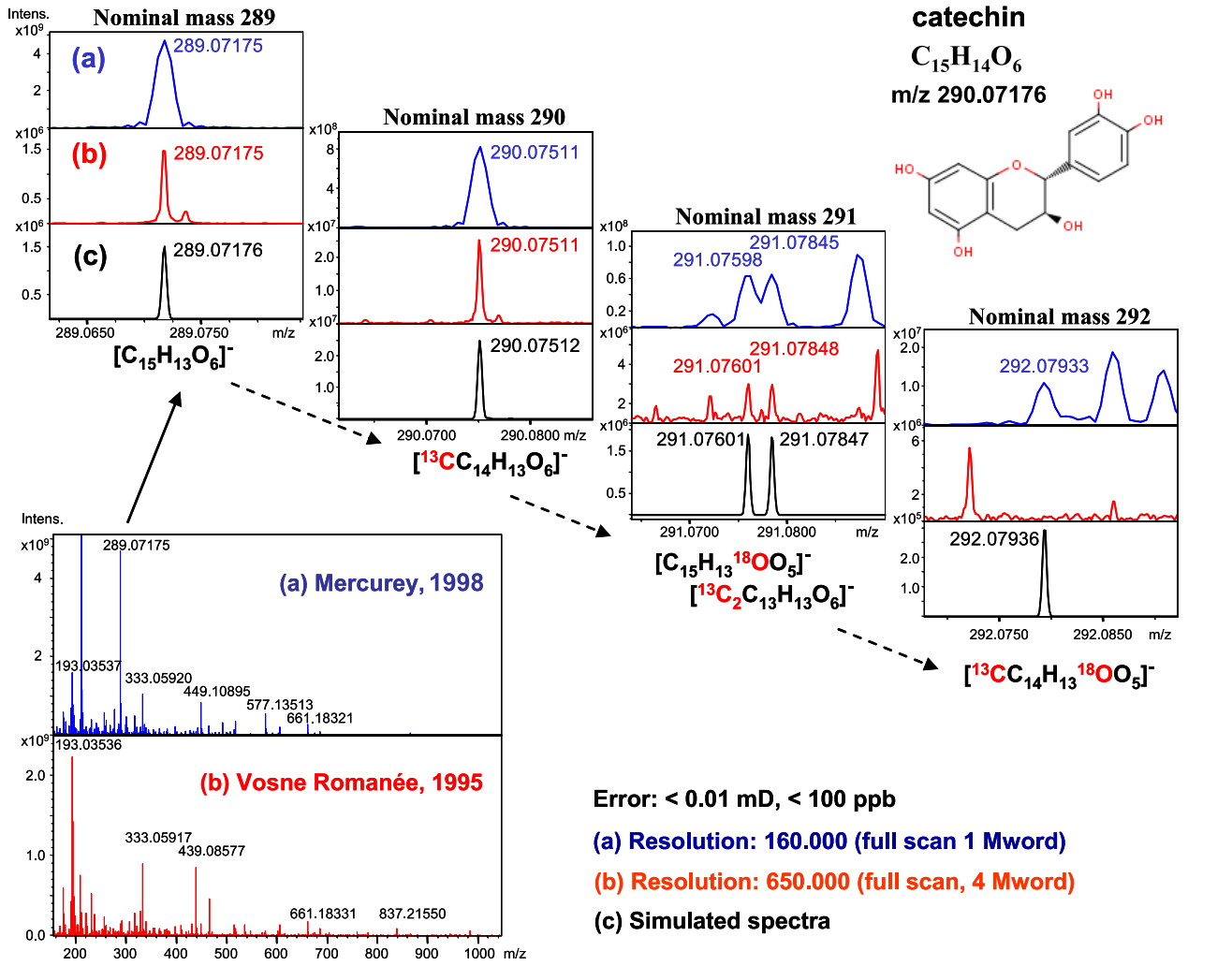

Fig. S1. ICR-FT/MS spectra of a Mercurey 1998 and a Vosne Romanée 1995 in electrospray-negative mode from *m/z* 200 to 1,000. The mass peak 289.07178 typically dominant in the Mercurey is represented in detail with corresponding resolutions of around 160.000 and 650.000 for the Mercurey and Vosne Romanée wines, respectively, and compared to the simulated spectrum, showing the presence of corresponding isotopologues at nominal mass *m/z* 290, 291, and 292. The presence of the isotopologue in the mass spectra is used to confirm the assigned elemental compositions of the signals in the spectra, and ultrahigh resolution combined to high-mass accuracy is needed to avoid false-positive assignments.

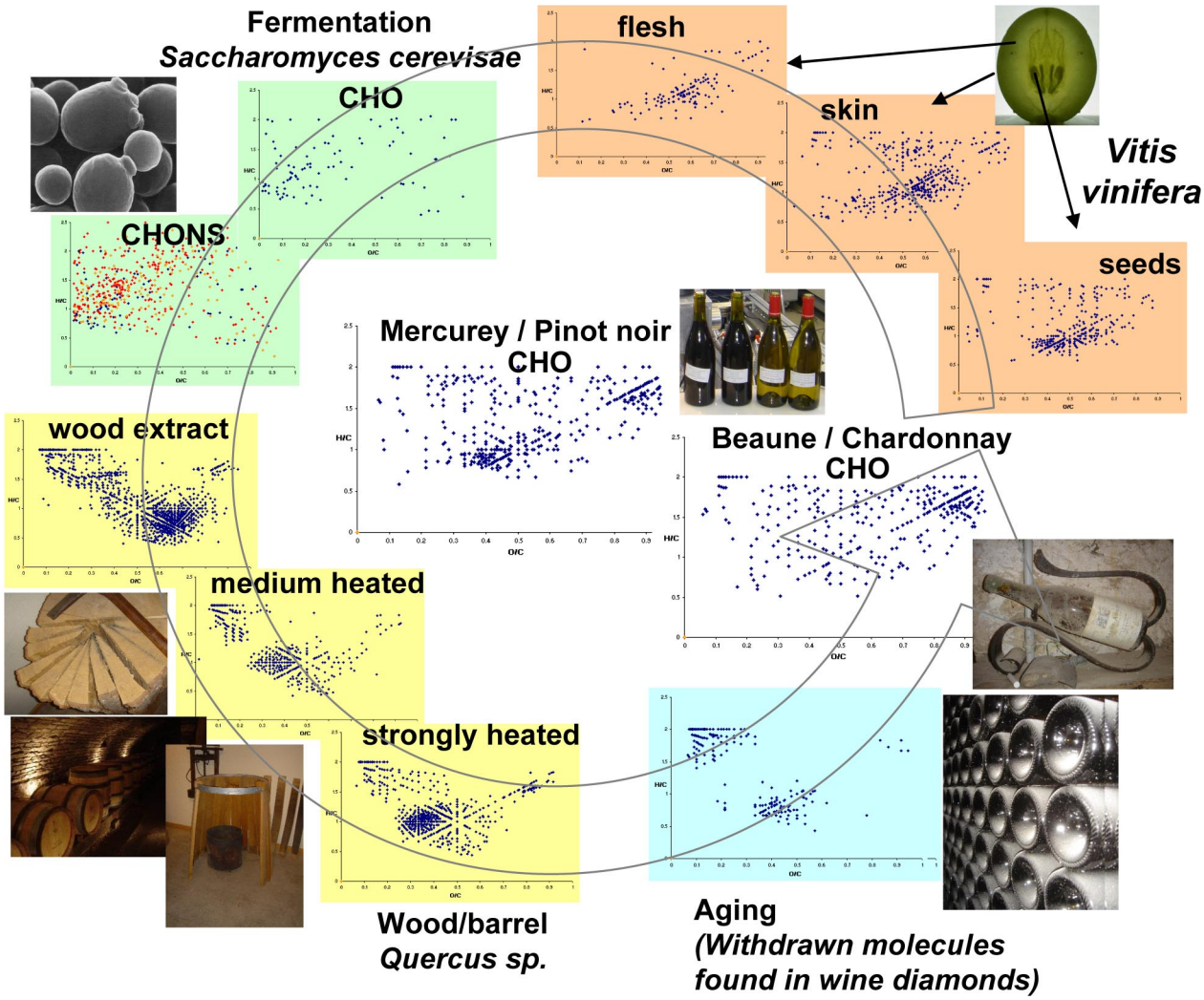

Fig. S2. Chemical spaces in the elaboration history of a wine; ''from vine to wine'' as visualized with the (O/C, H/C) van-Krevelen diagrams. Complementarities of the factors are visualized in the superimposition of the molecular footprints; interestingly, the fermentation step has much more importance in the CHON and CHONS space.

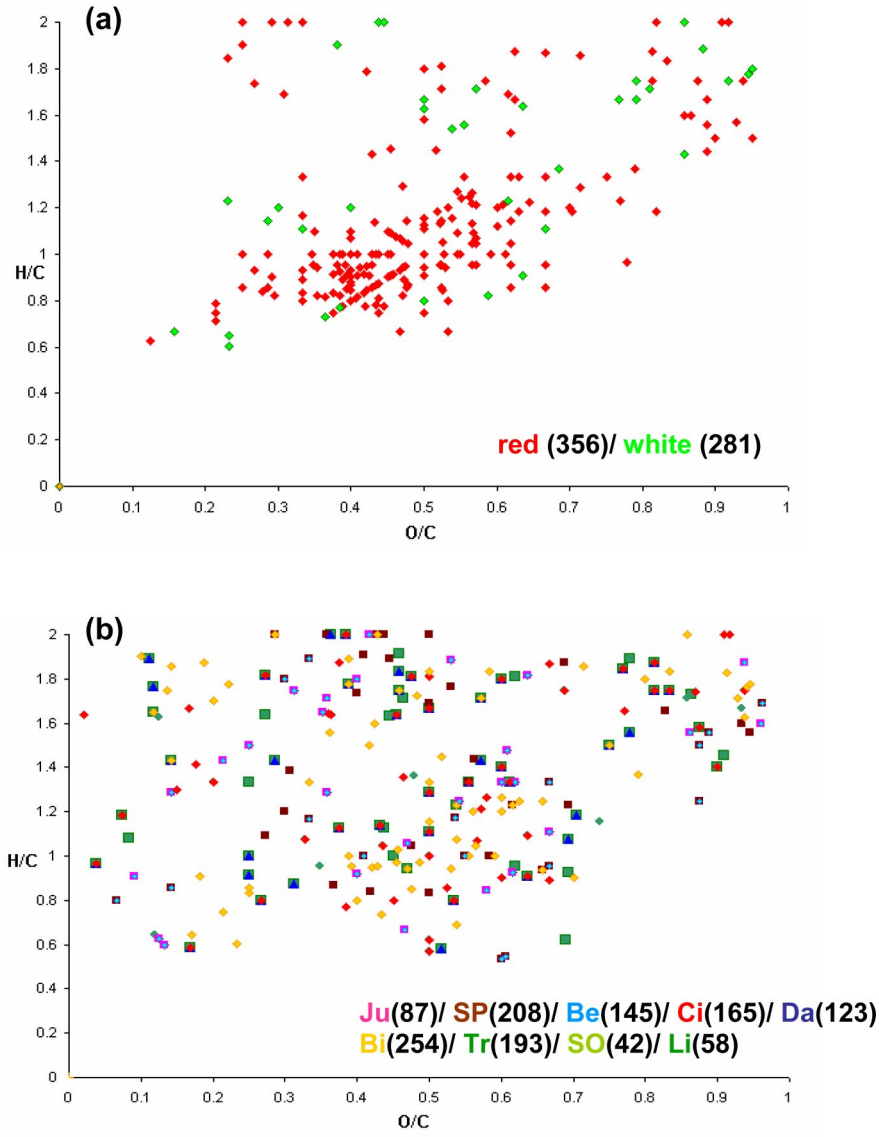

Fig. S3. van Krevelen representations of discriminant masses (highest correlation coefficients) for (*a*) red and white wines from the Tonnellerie 2000 experiment, and (*b*) wines sorted according to the forests of origin of oaks used for the barrels they were aged in, regardless of the species: (Ju) Jupilles, (SP) Saint Palais, (Be) Bertrange, (Li) Limousin, (SO) Sud Ouest, (Tr) Tronçais, (Ci) Citeaux, (Da) Darney, (Bi) Bitsch. Values in brackets indicate the total numbers of discriminant masses for each class

Other Supporting Information Files

Table S1