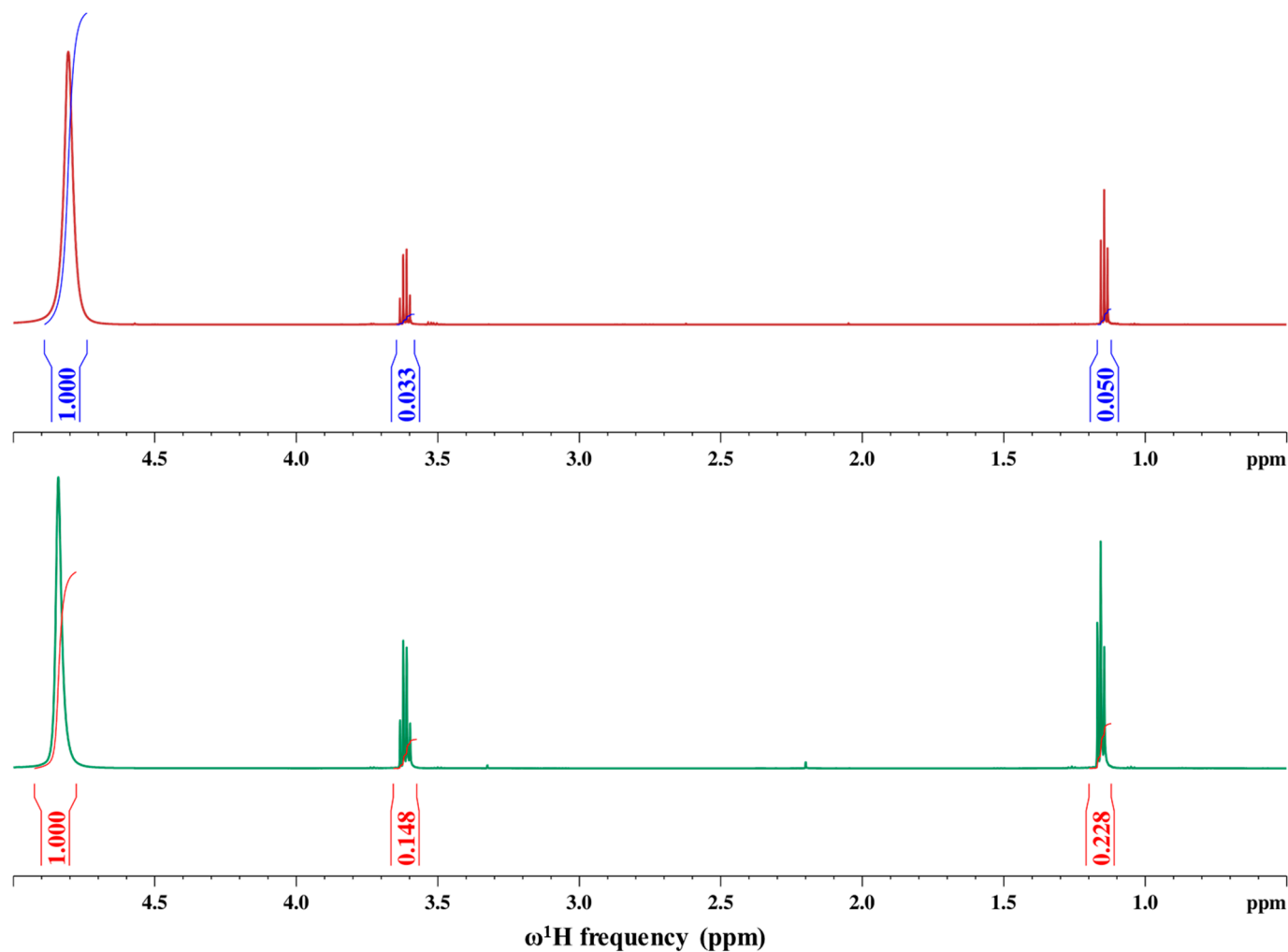
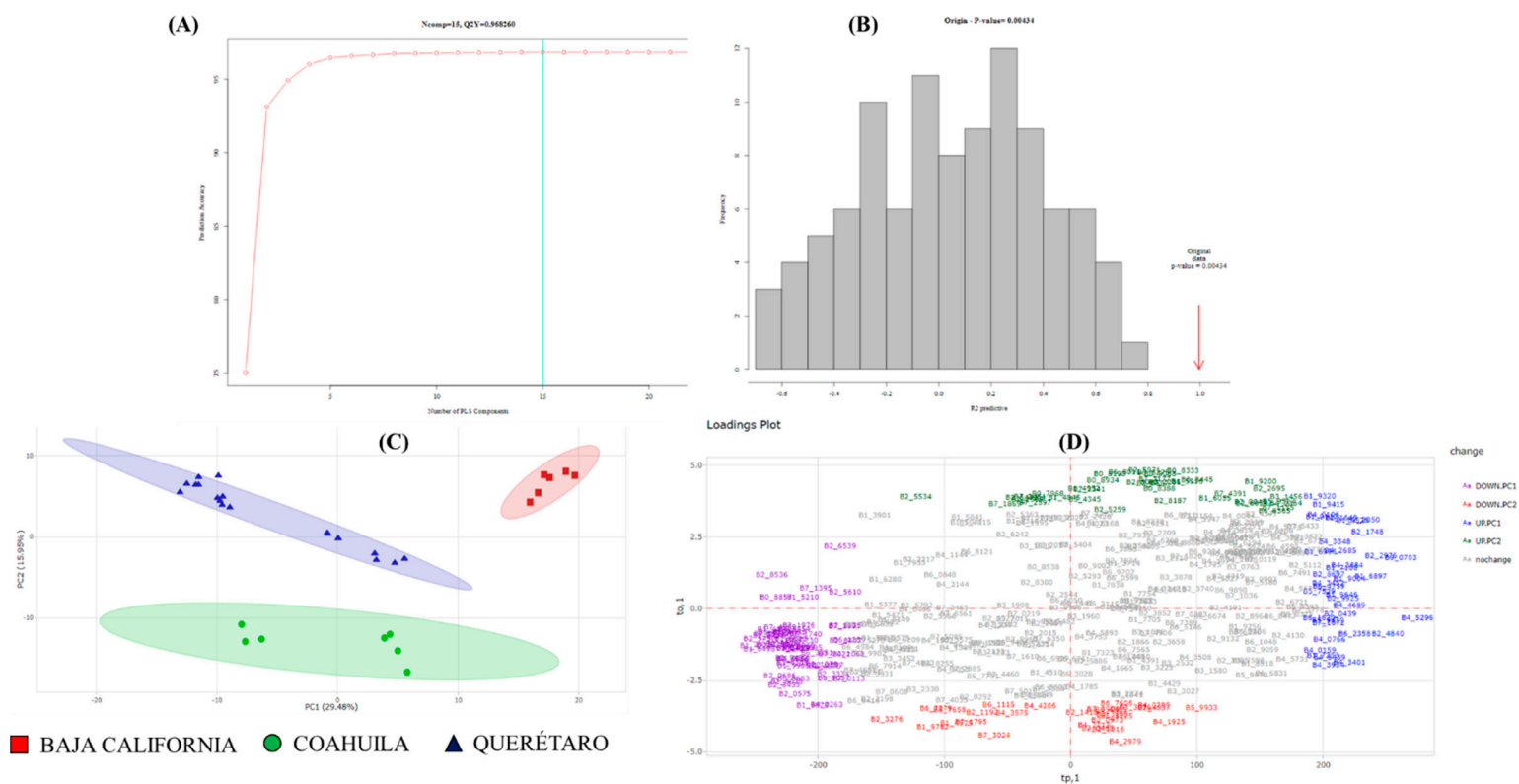


## Supplementary Materials

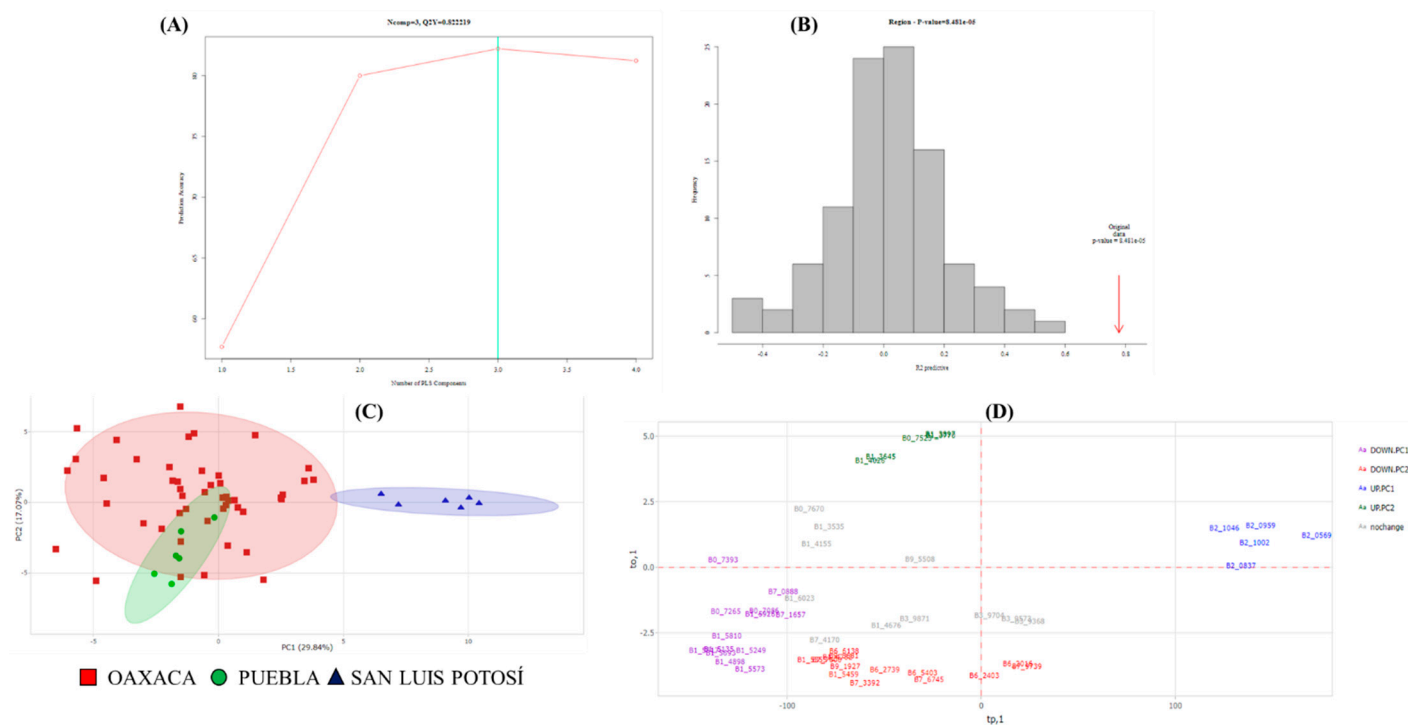


**Figure S1.** Standard direct-excitation one-dimensional proton nuclear magnetic resonance spectra of a wine (red) and mezcal (green) representative sample. Signal integration of intense water (4.83 ppm) and ethanol CH<sub>2</sub> (3.51 ppm) - CH<sub>3</sub> (1.14) spin systems is the starting point to predict effective power level of suppression off-resonance shaped pulses, applied in the <sup>1</sup>H<sub>2</sub>O presat NMR: 1D single pulse NOESY experiments, needed to produce NMR outliers (Figure 1, Main text) used

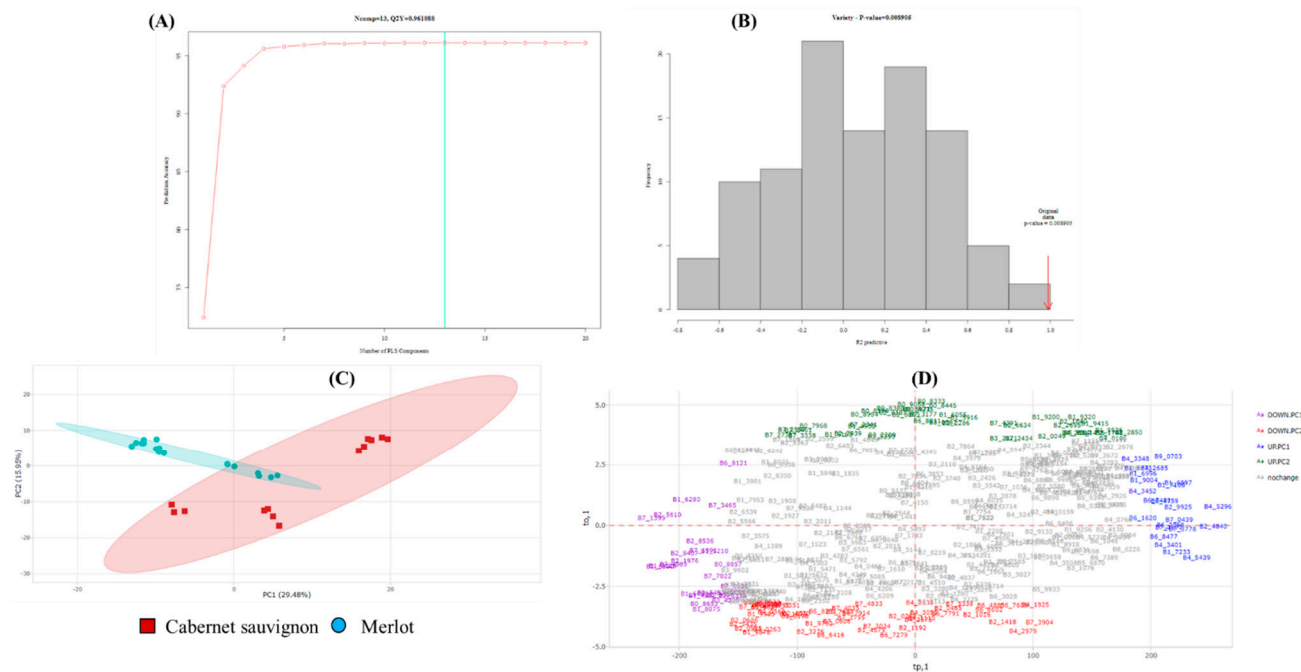
in MSA. Relative ethanol signal integration with respect water resonances reflect the different %ABV content in both spirits, that in turn defines the off-resonance shaped pulses amplitude differences in each case:  $8.19 \times 10^{-4}$  W (for wine samples) and  $1.18 \times 10^{-3}$  W (for mezcal samples).



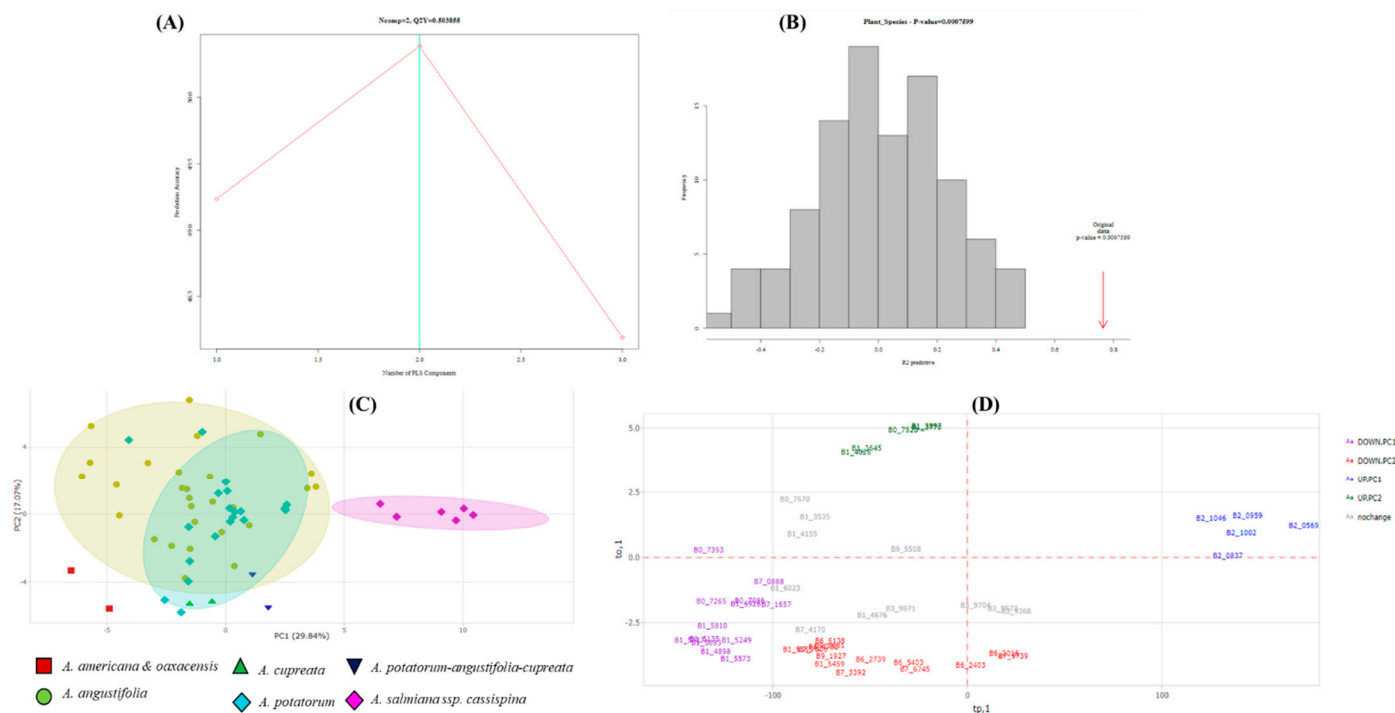
**Figure S2.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of wines' regional supervised discriminative analysis presented in Figure 2 top, main text.



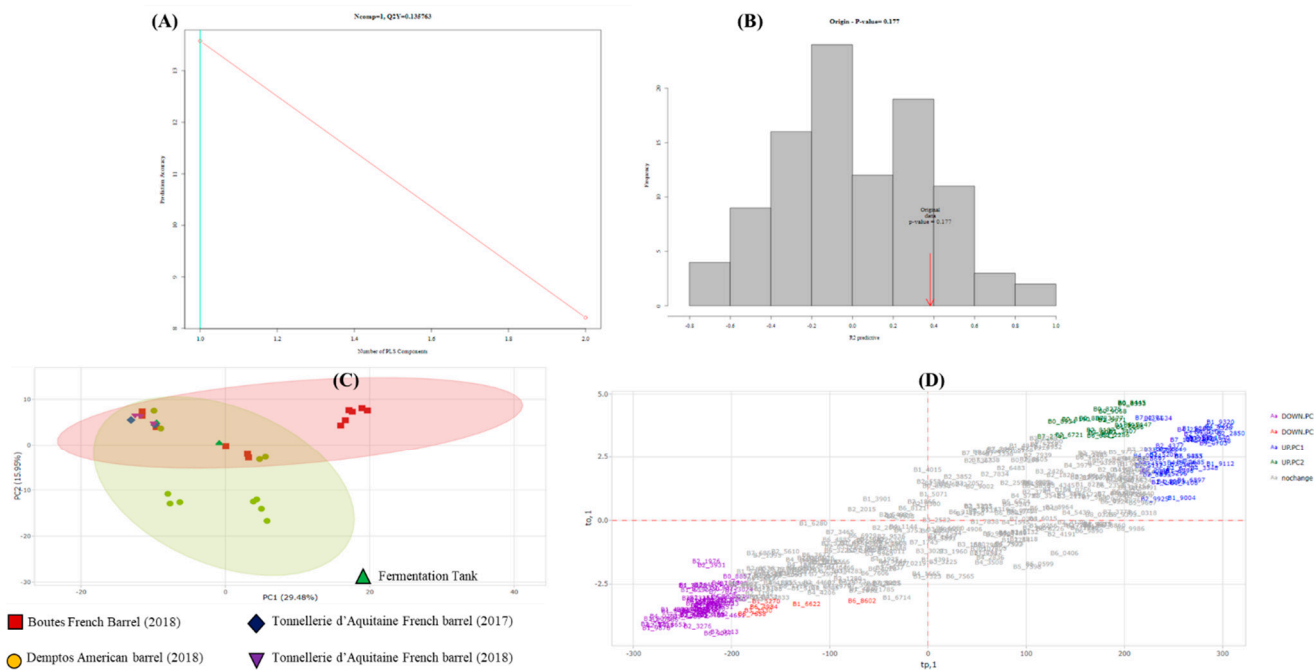
**Figure S3.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of mezcals' regional supervised discriminative analysis presented in Figure 2 bottom, main text.



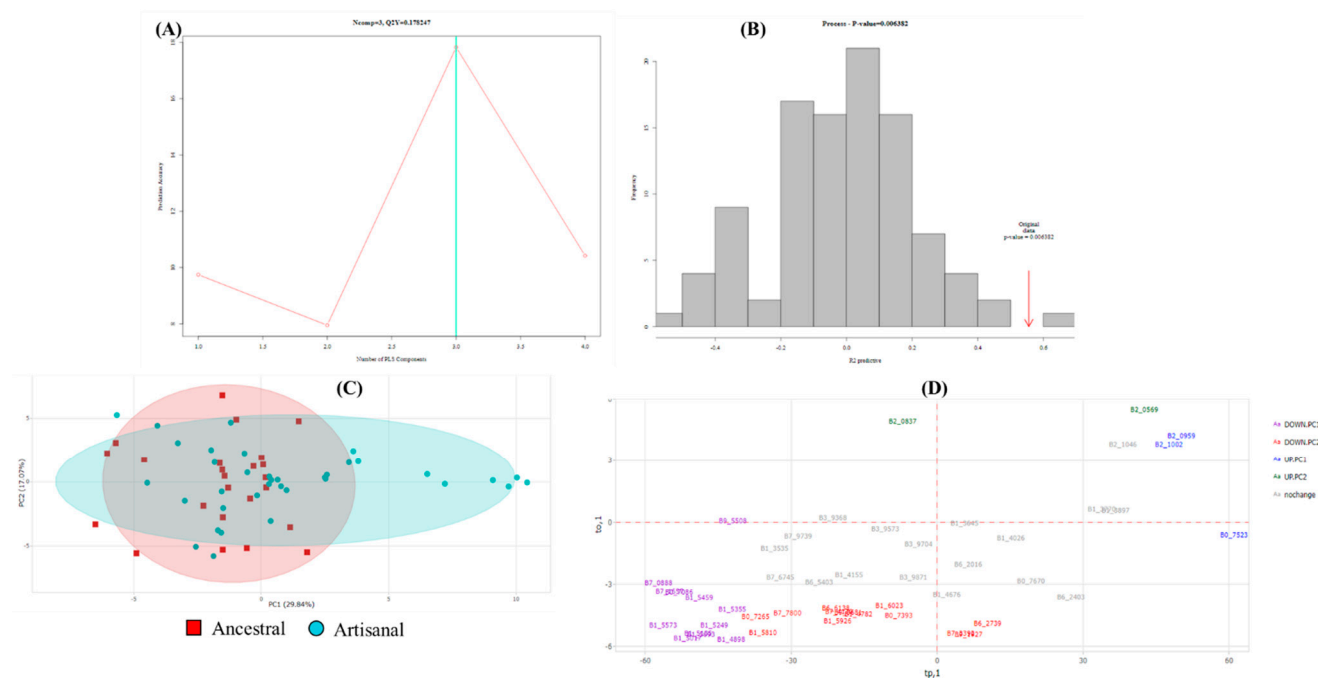
**Figure S4.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of wines' varieties supervised discriminative analysis presented in Figure 3 top, main text.



**Figure S5.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of mezcal species supervised discriminative analysis presented in Figure 3 bottom, main text.



**Figure S6.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of wines' ageing processes supervised discriminative analysis presented in Figure 4 top, main text.



**Figure S7.** Prediction accuracy curves as a function of PLS components, permutation tests, Principal Component Analysis (PCA) obtained from the same NMR data matrix and OPLS-DA loading plots of mezcal's manufacturing processes supervised discriminative analysis presented in Figure 4 bottom, main text.