Supporting information

1.1. Detection of condensed tannins in red wine samples by the Bate-Smith assay

Grape seeds oligomeric proanthocyanidins (condensed tannins) concentrations in red wine were also determined using the Bate-Smith assay (Stadler et al., 1982) as a validating methodology. Red wine samples were diluted with ultrapure water. Two separate 15 ml test tubes were prepared for every type of red wine, and 4 ml of diluted red wine, 2 ml of ultrapure water, and 6 ml of hydrochloric acid were added in each test tubes. One test tube was water bathed at 100 □C for 30 minutes and the other tube (blank) was stored in dark for the same time. After the heating, 1 ml of ethanol was added to each tube and tubes were stored in dark until fully cooling down. The absorbance of each sample was acquired in a spectrophotometer at 550 nm using ultrapure water as the blank. The absorbance difference was then multiplied 19.33 to calculate the final concentration of proanthocyanidins in red wine samples, and the concentration was expressed in g CE•L-1 (Catechin Equivalence).

1.2. Analysis of grape seed oligomeric proanthocyanidins, adenine, and their correlation.

Grape seeds oligomeric proanthocyanidins (i.e., condensed tannin) with different concentrations (500-2250 mg/l) and DNA fraction (i.e., Adenine) with different concentrations (2.5-45 μg) were initially dissolved into 15% ethanolic water solution. Then, 10 μl of condensed tannin solution/adenine was instilled onto the surface of AgNPs mirror substrate. After 5-minute incubation, the sample was air-dried for Raman measurements.

All Raman intensities were averaged from at least eight replicates and standard deviation was recorded. For condensed tannin, adenine, the peak at 733 cm^{-1} was chosen and the average Raman intensity was plotted as a function of concentrations of condensed tannin and adenine, respectively. Linear correlations were performed for both condensed tannin and adenine and calibration curves were generated. The correlation was also performed between the concentration of condensed tannin and adenine at the same Raman intensity of 733 cm^{-1} to determine the linear relationship of two wine components. In the direct red wine analysis, the amount of condensed tannins was determined based on the preceding standard curves and the Raman intensity of 733 cm^{-1}. Calculated concentration of condensed tannins was validated with the Bate Smith assay and the recovery value (i.e., RV%) was calculated based on the following equation:

$$RV\% = \left(\frac{Conc.\ of\ condensed\ tannin_{\ SERS}}{Conc.\ of\ condensed\ tannin_{\ Bate-Smith}}\right) \times 100$$

The concentration of adenine in red wines was hypothesized to indicate the amount of condensed tannins in red wines. To demonstrate the relationship, Raman intensity of adenine and condensed tannins were plotted as a function of their concentrations, respectively (SI 2). After the comparison of two plots, a proportional correlation was observed between adenine and condensed tannins in Figure 2 (C) along with the coefficient of determination (0.9968). Additionally, a mathematic model was presented in Figure 2 (C) to predict the concentration of condensed tannins in red wines based on the concentration of adenine detected using SERS.

Three red wine samples within different quality levels, Corley Family Cabernet Sauvignon State Lane Yountville, 2014 (Corley, high rating), Chateau de Chantegrive Graves, 2014 (Chateau, high rating), and Gallo Family Vineyards Hearty Burgundy (Gallo, acceptable rating) were analyzed using the AgNPs mirror substrate and the spectra were shown in Figure 3 (A). Noticeable differences within three wine samples were observed and further confirmed in the principle components analysis (i.e., PCA) in Figure 3 (B). Distinctions were presumably due to different

quality levels and the varied enological nature of three red wines, including origins, viticulture, species, fermentation process, and ages. Nevertheless, even though spectral disparity was observed, signature peaks of adenine still dominated in all red wine spectra. The concentrations of adenine were calculated in each red wine according to the peak intensity at 733 cm^{-1} and the calibration curve (showed in SI). In Figure 3 (C), the concentrations of condensed tannins were estimated via the equation,

$$C_{condensed\ tannin} = C_{adenine} \times 37.2 + 450.53$$

Within three red wines, Corley family Cabernet Sauvignon showed the highest concentration of condensed tannins, followed with the Chateau de Chantegrive and the Gallo Hearty Burgundy. To validate the estimation, a standard UV-spectrophotometer based Bate Smith assay was applied to determine concentrations of condensed tannins in three red wines. After the calculation, a similar tendency of the condensed tannins concentrations in red wines was observed between SERS and Bate Smith Assay in Figure SI2, which indicated that the SERS method is reliable in quantification of condensed tannins.

Therefore, foregoing results suggested that the adenine, a DNA based molecule released along with condensed tannins during the enological process from grapes, can be used as a SERS indicator to estimate the concentration of condensed tannins in red wines. Furthermore, since the amount of condensed tannins is responsible to the reception of astringency (Waterhouse, A. L., Sacks, G. L. and Jeffery, 2016), which is reported to be positively related to the wine quality, the determination of adenine using SERS can provide a quick predication of the overall quality of red wines.

To be noted, even though Bate Smith method was considered as a validation in this study, the SERS also showed many advantages in the experimental practice such as faster operation (i.e., the whole analysis only took less than 10 minutes including the sample preparation) and simpler preparation, compared to the Bate Smith.

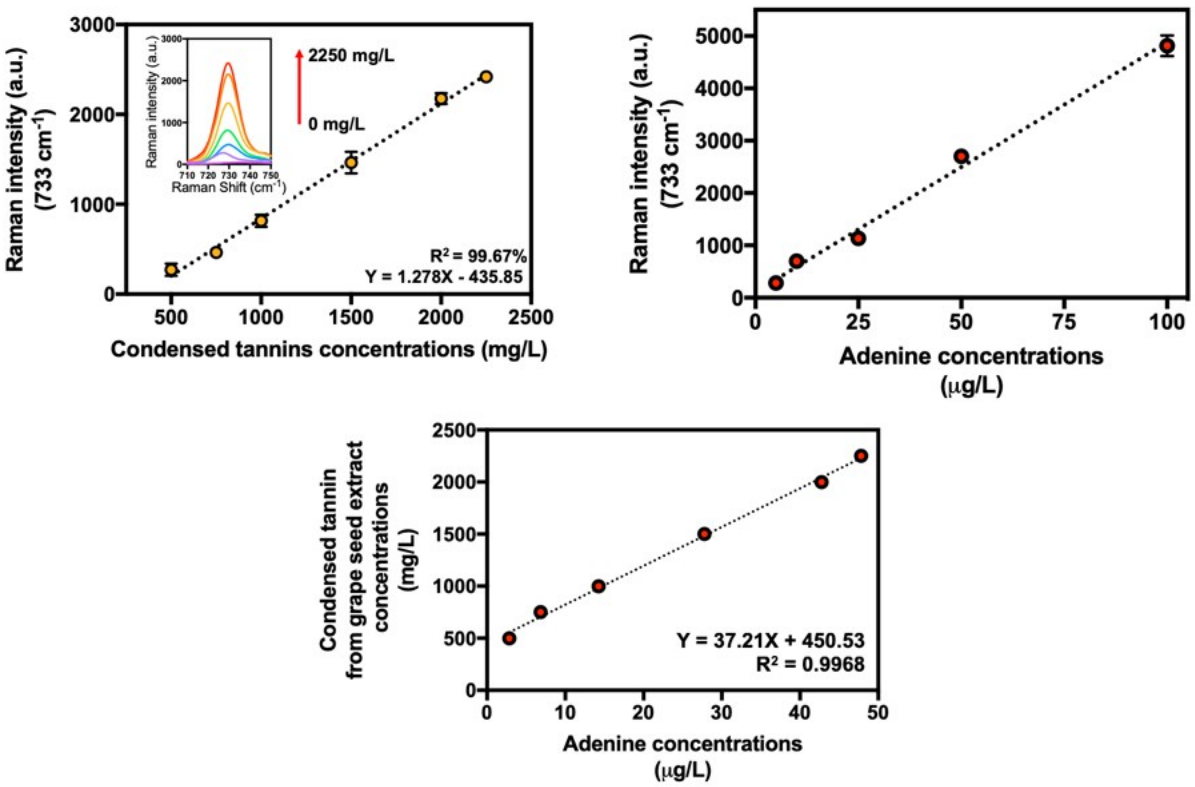

Figure SI1. Plots of Raman intensity as a function of concentrations of oligomeric proanthocyanidins and adenine, respectively. Concentration correlations between condensed tannin from grape seed extract and adenine.

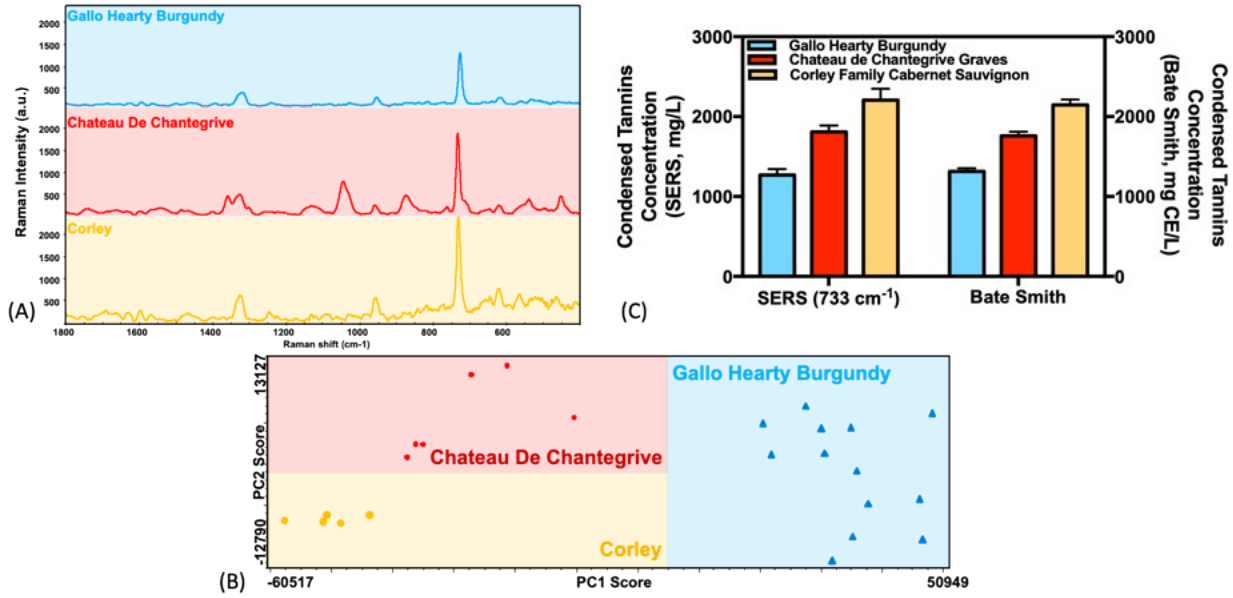

Figure SI2. (A) spectra for three wines (B) PCA differentiation of three wines (C) estimation of concentration of condensed tannin in wines and the validation through Bate Smith UV spectroscopic method

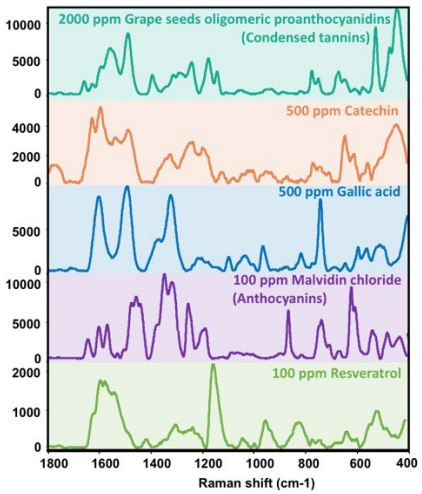

Figure SI3. SERS spectra of analyzed wine chemicals.