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Research Article

The Degree of the Physical Maturation of Wine Using Laser Raman Spectroscopy

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Abstract: The study aimed to explore the most appropriate physical maturation periods of wines made from different raw materials. Eight wine samples stored for different periods including a hull-less barley wine, a maize wine, a rice wine and a glutinous rice wine were examined using laser Raman spectroscopy. The Raman intensity ratio at 3200/3400 cm was used as an indicator of the degree of physical maturation of the tested samples. Results showed that the most appropriate physical maturation periods were 15, 30 and 10 and 20 months, respectively for the hull-less barley wine, the maize wine, the rice wine and the glutinous rice wine, respectively; continued aging beyond these periods had almost no effect on physical maturation, except that it did lower the physical maturation of the glutinous rice wine. The maturation process for the maize wine was rapid and sustainable and the degree of maturation was excellent. Moreover, the Raman intensity ratio at the end of maturation was about 3-4 times that of the other wines; this finding was consistent with the sensory evaluation results. A good correlation between the Raman intensity ratio and the gross value for the total acidity and amino acid content was also found for the wines investigated.

Keywords: Physical maturation, Raman intensity ratio, Raman spectroscopy, wine

INTRODUCTION

Generally, it is believed that the maturation process of wine includes two processes: the physical maturation process consisting mainly of hydrogen bonding between ethanol-water and other constituent molecules and the chemical maturation process which includes oxidative acidification, hydrolysis and acetylation and other chemical reactions (Wang *et al*., 1990; Zhang, 2003). Research on the degree of physical maturation in practice concerns studying the extent of order in the alcoholic solution, namely the degree of hydrogen bonding among the ethanol-water-constituent molecules and whether there is more and larger bonding groups formed with a higher degree of bonding. As a consequence, proton exchange is reduced and there is a reduction in the irritating effects of ethanol and taste becomes milder indicative of a more complete aging maturation (Guo, 1992; Han and Cui, 2005; Piggott *et al*., 1989). Given that about 80% of wine-making ingredients are water-based, laser Raman spectroscopy has generally been used to investigate the water hydroxyl stretching vibrations. In Raman spectra, the vibration peak near 3200/cm is due to strong hydrogen bonding and the vibration peak near 3400/cm represents non-hydrogen bonding or a weak hydrogen bonding product. Generally, the intensity ratio at 5°C of the two hydroxyl stretching vibration peaks near 3200/cm and 3400/cm is used as an index (maturation index) of the degree of hydrogen bonding (O-H···O) in wine. A high ratio indicates a high degree of bonding of the alcohol-water hydrogen bonds in the wine solution and a high degree of physical maturation (Nose *et al*., 2004, 2005a).

In this study, four wines (hull-less barley wine, maize wine, glutinous rice wine and rice wine, which are similar to Japanese sake) made by wine companies in Sichuan Province of China were tested by laser Raman spectroscopy to study the physical maturation of the wines to establish appropriate ageing times for the wines and, thus, to minimize the storage period and corresponding storage costs for the wine companies.

MATERIALS AND METHODS

Materials: Hull-less barley wine (HBW): The raw material for HBW consisted of 70% hull-less barley rice and 30% glutinous rice. The alcohol content was 12-14% (v/v). HBW01 signifies a storage time of one month and HBW05 indicates a storage time of five

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Table 1: The chemical parameters of the wine samples tested g/L (except pH)

Wine sample	Non-sugar solids	Total sugar	Total acid	Amino nitrogen	pH	Wine sample	Non-sugar solids	Total sugar	Total acid	Amino nitrogen	pH
HBW01	31.1	38.6	7.6	0.73	4.3	MZW01	18.7	34.7	7.2	0.55	4.6
HBW05	31.1	38.6	7.6	0.76	4.2	MZW05	19.6	33.1	7.3	0.53	4.5
HBW10	31.9	37.1	7.9	0.76	4.3	MZW10	19.8	32.3	7.5	0.53	4.4
HBW15	31.9	36.3	7.9	0.71	4.5	MZW15	19.8	30.6	7.6	0.47	4.5
HBW20	32.7	36.1	8.0	0.68	4.5	MZW20	20.1	30.6	7.7	0.45	4.3
HBW24	33.1	36.1	8.0	0.66	4.5	MZW24	21.6	30.2	7.7	0.46	4.3
HBW30	33.3	35.4	8.2	0.63	4.4	MZW30	21.7	30.1	7.9	0.45	4.4
HBW36	33.1	35.4	8.2	0.63	4.2	MZW36	21.3	28.4	7.9	0.45	4.4
RCW01	22.3	52.8	7.8	0.49	4.3	GRW01	26.4	67.5	7.9	0.46	4.2
RCW05	23.8	49.6	7.8	0.48	4.3	GRW05	26.8	65.2	8	0.43	4.4
RCW10	23.8	46.1	7.9	0.48	4.4	GRW10	26.9	61.1	8.2	0.40	4.2
RCW15	24.5	44.5	8.3	0.45	4.3	GRW15	27.7	58.8	8.2	0.37	4.2
RCW20	24.5	42.7	8.5	0.42	4.1	GRW20	27.7	56.2	8.5	0.35	4.1
RCW24	25.1	42.7	8.5	0.42	4.1	GRW24	28.1	56.2	8.7	0.36	4.3
RCW30	25.9	40.4	8.6	0.41	4.2	GRW30	27.8	56.0	8.9	0.33	4.1
RCW36	25.8	38.3	8.8	0.42	4.1	GRW36	27.1	55.3	9.3	0.34	4.1

months and so on. Eight HBW samples, corresponding to different storage times (1, 5, 10, 15, 20, 24, 30 and 36 months, respectively), were collected (similarly for the wines below).

Maize wine (MZW): The raw material for MZW consisted of 70% of the embryo-less yellow maize (2-3 mm) and 30% of glutinous rice. The alcohol content was 12-14% (v/v).

Rice wine (RCW): Japanese rice served as the raw material. The alcohol content was 14-15% (v/v).

Glutinous rice wine: Glutinous Japanese rice served as the raw material. The alcohol content was 16-17% (v /v).

Non-sugar solids, total sugar, total acid, amino nitrogen content and pH for the wine samples are listed in Table 1. The measurement of these parameters was carried out according to the relevant methods in the Chinese national standard-"Yellow Wine" (GB/T13662-2008) (Guo *et al*., 2008).

Apparatus: A laser Raman microscope (DXR; Thermo Fisher Scientific, USA) was used because of its high degree of automation, modular design and user-friendly operation. The system featured an Argon ion laser operating at 780 nm.

Methods: Wine samples were examined at 5°C using 18 mW of laser power over the range 70-3500/cm. The raw spectral data were subjected to Savizky-Golay polynomial smoothing using Origin 8.5 software to identify the Raman intensities of the stretching vibration peaks of the hydroxyl groups near 3200/cm and 3400/cm and then to calculate the intensity ratio of the peaks at 3200/cm 3400/cm as a measurement index of the degree of physical maturation of the wine (Nose *et al*., 2005b). All measurements were carried out in triplicate.

RESULTS AND DISCUSSIONS

The Raman spectra were obtained at 5°C for each sample. Figure 1 is the Raman spectrum of HBW10 (the abscissa represents the Raman shift and the ordinate represents the relative intensity of the Raman signal). This figure includes eight Raman peaks for ethanol and water at 3100 to 3500/cm. Raman spectra of other samples in this spectral region were similar with only differences occurring in the peak intensities and slight differences in the peak positions. Given that the vibration peaks near 3200/cm originate from the strong hydrogen bonding products of water and the vibration peaks near 340/cm were from non-hydrogen bonding or weak hydrogen bonding products of water, the characteristic peaks within the range 3100 to 3500/cm were the focus of this study.

In spectrochemical analysis, the Savizky-Golay polynomial smoothing function is widely used to reduce noise and errors, thus improving the signal to noise ratio and spectral quality (Xu and Shao, 2004). Using Origin 8.5 and the Savizky-Golay smoothing method, the Raman spectral data of the different wine samples were subjected to smoothing, three times on average. After smoothing, two distinct peaks could be observed for the vibration bands of OH within the region 3050/cm to 3500/cm (near 3200 and 3400/cm). Figure 2 shows the spectrum of HBW10 within the region 3000/cm to 3500/cmafter smoothing. The calculated Raman intensity ratios (3200/3400/cm) corresponding to different storage periods for the wine samples are shown in Fig. 3 and 4. Figure 3 shows the Raman intensity ratios *vs*. different storage periods for RCW and GRW and Fig. 4 shows those for HBW and MZW.

In Fig. 3, after the RCW was stored for one month, the Raman intensity ratio was 0.43. The ratio value then increased to 0.47 at 5 months storage and continued to increase to around 0.55 for 10 months storage. Thereafter, the Raman intensity ratios remained relatively constant at 0.54–0.56 after 15, 20, 24 and 36

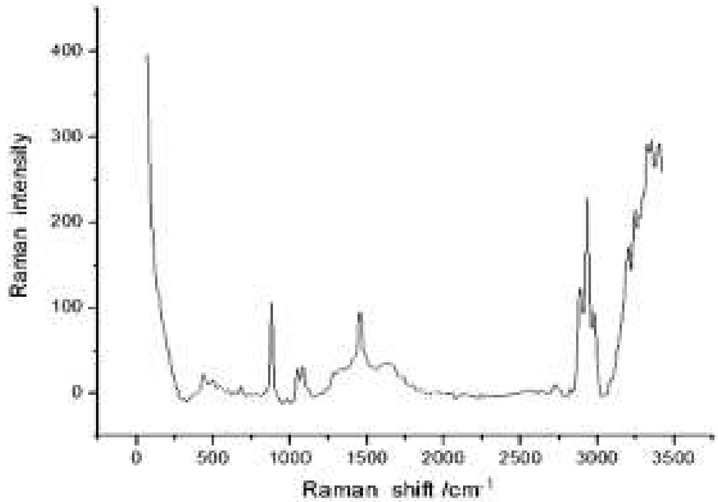

Fig. 1: Raman spectrum of hull-less barley wine (HBW) after ten months of storage

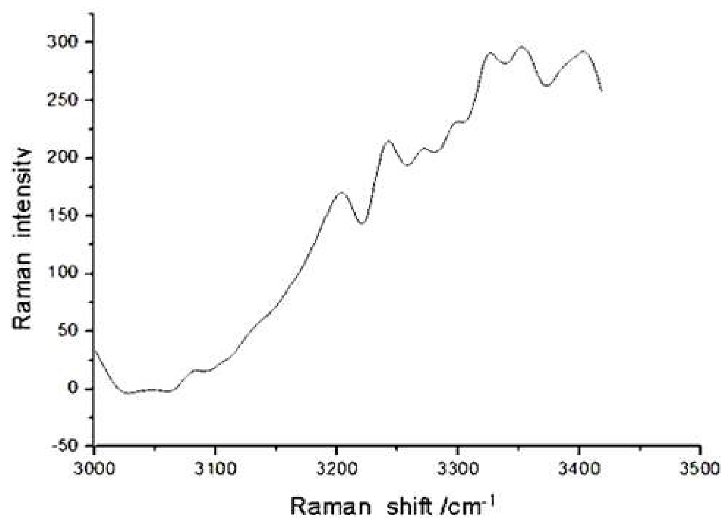

Fig. 2: Savizky-Golaypolynomial smoothed Raman spectrum of Hull-less Barley Wine (HBW) after ten months of storage (3000/ cm to 3500/cm)

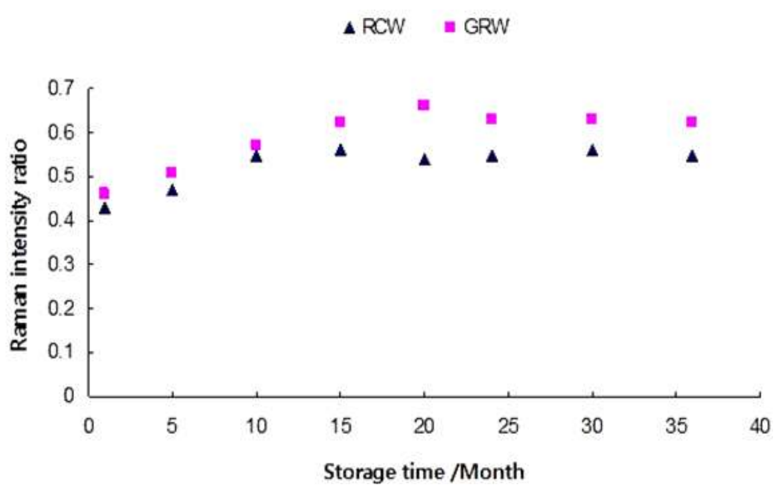

Fig. 3: Raman intensity ratios of rice wine (RCW) and Glutinous Rice Wine (GRW) for different storage times

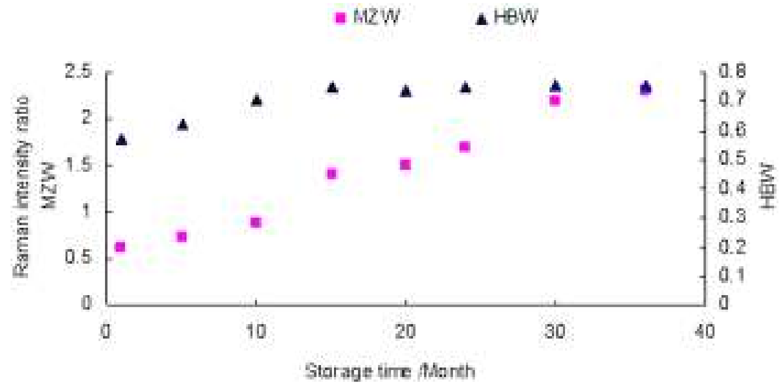

Fig. 4: Raman intensity ratios of maize wine (MZW) and hull-less barley wine (HBW) for different storage times

months storage, the values being not that much different from that at 10 months significantly ($p > 0.01$), indicating that the degree of physical maturation of RCW was optimal after about 10 months of storage. Compared with RCW, the GRW gave a different time profile for the Raman intensity ratios. The optimal time to reach the highest degree of physical maturation was 20 months (Raman intensity ratio, 0.66). Thereafter, the Raman intensity ratios for GRW decreased, the values at 24, 30 and 36 months being 0.63, 0.63 and 0.62, respectively, which were significantly different from that of 20 months ($p<0.05$); but there was no significant difference between those of 24, 30 and 36 months ($p>0.01$). These results showed that the most appropriate aging time for physical maturation of GRW was 20 months. With further ageing, the degree of intermolecular hydrogen bonding of the alcohol-water-other constituents would weaken and/or the aggregations would become smaller as revealed by the intensity ratio (3200/cm/3400/cm) values which levelled off at 0.62-0.63. This further ageing did result in a mild taste for the GRW.

The biggest difference between the GRW and the RCW was that the amylopectin content of the GRW (over 96%) was significantly higher than that of the RCW (about 75%), thus the amount of oligosaccharides in the GRW was also more than that in the RCW. As listed in Table 1, the total sugar contents of the GRW were higher than those in the RCW. Table 1 also showed that the GRW had a higher total acid content than that of the RCW. Based on an analysis of the differences in the degree of physical maturation of the RCW and the GRW, the oligosaccharides (maltose, panose, maltotriose, maltotetraose, etc.) in the GRW might participate in the formation of hydrogen-bond-associated aggregates of alcohol-water. However, after a certain storage period, these oligosaccharides would react with other substances, such as organic acids and amino acids (e.g., Maillard reaction) in the GRW, resulting in a change in the hydrogen bonding aggregates, thus affecting a decrease in the Raman intensity ratios.

Figure 4 shows the Raman intensity ratio change with storage time for HBW and MZW. The Raman intensity ratio for HBW increased gradually from one month to 15 months; for 15 months of storage, the ratio attained the highest value of 0.75, which then remained stable (0.74-0.75) over longer storage periods and without significant differences ($p>0.01$) compared with storage at 15 months. These results demonstrated that an appropriate physical maturation period for HBW was 15 months; after 15 months, further ageing had little effect on physical maturation.

The results for MZW were the most interesting for all samples tested, the Raman intensity ratio being 0.61 after one month's storage, a value which was higher than that for RCW (0.55) after 36 months and for GRW (0.57) after 10 months. Thereafter, the Raman intensity ratios for MZW increased monotonically with storage time. After 10 months storage, the Raman intensity ratio exceeded the maximum values of the other three wines and reached 2.2 and 2.3 after 30 months and 36 months (the difference between these two values was not significant ($p>0.01$)), respectively, values which were about 3 to 4 times those of the other three wines. These results showed that for the MZW samples, hydrogen bond association of alcohol–water–other constituent molecules was very favorable, the degree of bonding and/or the scale of aggregation gradually increasing with storage time. Consequently a suitable physical maturation period was 30 months, which was much longer than that for the other three wines. This finding was consistent with our preliminary findings in an organoleptic evaluation. Namely, after MZW was stored for a year, there was almost no irritating smell of alcohol (on sniffing) and the taste was soft and mild; accordingly, the organoleptic evaluation result was better than that for the other three wines (Table 2) (Li *et al*., 2010). Yellow maize grain contains carotene, folic acid, niacin, flavonoids, vitamin E, dimension B, vitamin A, riboflavin and other substances (Xu *et al*., 2010). These substances have phenolic hydroxyl groups or carboxyl groups which can participate or enhance dynamic hydrogen-bond association between ethanol and water molecules in the wine and gradually increase the hydrogen bond association aggregation scale for wine over time. Therefore, the MZW, relative to the other wines, exhibited better physical ageing and

Table 2: Organoleptic evaluation of the wine samples tested after one year of storage※

Wine sample	HBW	MZW	RCW	GRW
Organoleptic evaluation score	67	78	64	69

※Higher scores indicated better quality; 100 points in total (the color (10 points), aroma (25 points), taste (50 points) and typicality (15 points))

maturation characteristics which gave rise to a soft mellow taste.

As listed in Table 1, the values for the total acidity and the amino acid content of the MZW were relatively small compared with those for the other three wines. However, the ageing characteristics of the MZW were good, which seemed to contrast with the good correlation between the Raman intensity ratio and the gross value for the total acidity and amino acid content (Nose *et al*., 2004). In fact, the results were consistent because this correlation analysis had to be performed for the same wine samples. Based on an analysis of the relationship between the Raman intensity ratio and the gross value for the total acidity and amino acid content of the tested wine samples, it was found that the MZW had the best correlation with a correlation coefficient of 0.97, while that for the HBW, the RCW and the GRW was 0.90, 0.72 and 0.69, respectively.

CONCLUSION

Using laser Raman spectroscopy, eight samples of a HBW, a MZW, a RCW and a GRW corresponding to different storage times were examined with a focus on spectral analysis of the characteristic water peaks within the range 3100 to 3500/cm. Using the Savizky-Golay polynomial procedure, the spectrum within this range was smoothed to obtain the Raman peak intensities near 3200/cm and 3400/cm. The Raman intensity ratio, 3200/cm/3400/cm, was used as a measure of the degree of physical maturation of the wine samples. The results showed that appropriate physical maturation periods for the HBW, the MZW, the RCW and the GRW were 15, 30, 10 and 20 months, respectively. Ageing beyond these maturation periods had almost no effect on physical maturation, except in the case of the GRW where the degree of physical maturation decreased. The maturation of the MZW was relatively fast and was sustained with excellent maturation performance. After the MZW was stored for 10 months, the Raman intensity ratio exceeded the maximum ratio values for the other three wines; and, at the end of maturation (30 months), the value was about 3 to 4 times those of the three other wines. These findings were consistent with the sensory evaluation results. It was further noted that there was good correlation between the gross value of the total acidity and amino acid content for the wines and Raman intensity ratio values.

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