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Determination of the Age of Sherry Wines by Regression Techniques Using Routine Parameters and Phenolic and Volatile Compounds

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This paper describes a study of the possibility of obtaining regression models by means of partial least squares (PLS) and multiple linear regression (MLR) that would enable us to correlate a series of parameters, such as the concentration of short-chain organic acids, higher alcohols, and phenolic compounds with the age of vintage Sherry wines or "añadas". The aim of this study is to characterize how these parameters evolve with aging. If this could be done, it would then be possible to guarantee the age of such wines using objective variables. A PLS regression model was established that allows the age to be predicted with a mean deviation of 1.6 years with respect to the age of the wines. In the case of the MLR, a model with 6 variables was obtained that gives a mean deviation of 3.3 years in the predictions.

KEYWORDS: Partial least squares; multiple linear regression; phenolic compounds; volatile compounds; wine; aging

INTRODUCTION

Most wines are consumed after a period of aging that may take place in wooden casks, in the bottle, or in both successively.

For many wines, this period of aging is a necessary stage in the production process. The effect of aging is to modify the various organoleptic properties of the wine, making some more and others less intense (*1*). This process implies a significant financial cost that must be recovered in the final price of the wine.

For this reason, it is of commercial interest to characterize the chemical reactions that take place during the processes of aging. The end purpose of such studies is to modify these processes so as to increase the more valuable characteristics and reduce the unwanted characteristics of the final wine.

In the case of aging in casks, the compounds extracted from the wood play a fundamental role in the properties of the wine. The study of these compounds has usually been performed employing hydroalcoholic solutions, kept in casks for specific but limited periods (*2*−*6*). Among the compounds extracted are vanillin and other aldehydes (*4*), benzoic acids (*7*, *8*), particularly gallic acid (*9*) and furan derivatives (*10*).

Using this approach, attempts have been made to correlate the concentration of various compounds present in wine, with its period of duration in wood. However, the results obtained have not been satisfactory because, in some cases, like vanillin, their final concentrations in the wine considerably exceed the quantities that could possibly be extracted from the wood during the aging (*4*). In others cases, such as the furan compounds, which are extracted in relatively large quantity from the wood, these are also included among the authorized additives employed in the production of some wines; therefore, their quantities, similarly, could not be correlated definitively with the duration of the aging of commercial wines in wood (*11*). Moreover, on some occasions, it has been found that the quantity of some compounds extracted from the wood undergoes decreases during the aging, probably because of reactions with other compounds present in the wine (*5*).

In studies aimed at determining the age of products of natural origin, the quantities of certain isotopes have often been monitored. This technique has also been employed with wine (*12*). However, the results have not been good, as a consequence of the short periods of time of such studies, and because it is necessary to know the quantity of isotopes in the original wines before aging, this technique could not be applied to wines that are already aged.

Thus, it has not been possible to find the correlation between the age of a wine and the concentration of a specific compound in the final wine. Given this, it is considered that the employment of chemometric techniques could be very useful, because it would be more logical to find correlations between the age of a wine with a series of values corresponding to various parameters related to the processes of aging. Ortiz et al. have obtained such a correlation for a series of Port wines of up to 27 years of age (*13*). Employing PLS, they were able to devise a model of the evolution of the wine, taking as their base the

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routine analytical parameters, the concentration of polyalcohol-type compounds, volatiles, and metals, together with measurements related to the composition of phenolic compounds. Using PLS and the headspace compounds analyzed by solid-phase microextraction and GC/MS, Watts et al. (*15*) have obtained functions for determining the age of aged Cognacs. Three methods of regression were studied by Pérez-Coello et al. (*16*) for predicting the years of storage in bottles of Spanish white wines, by means of the analysis of volatiles.

Using multivariate regression techniques to study the evolution of analytical parameters during wine aging could, first, lead to the production of a model of wine evolution that could later be applied to determine the age of wines. Second, it could help to explain the chemical phenomena that take place during the aging process.

As already mentioned, the aging of wines in oak barrels is a process in which the organoleptic properties of the wine are modified as the result of a series of reactions whose effect is to strengthen certain desired characteristics while reducing or eliminating other unwanted ones. This process has considerable significance for the price of the wine, because the aging wine represents capital locked up for the duration of the process and this financial burden is carried by the producer. Nevertheless, old wines of high quality have always been sought after by certain consumers, although it must also be recognized that the typical wine consumer today is increasingly more knowledgeable and demanding and, before purchasing, requires a wine to be duly documented and authenticated with respect to its process of production and years of aging. Recently, the Regulatory Council of the Jerez-Xérès-Sherry Denomination of Origin has created two special categories of Sherry wines of certified age: wines more than 20 years of age (V.O.S.), and wines more than 30 years of age (V.O.R.S.). This classification is intended to give these wines an official certification so that their age and extraordinary quality is recognized in the market.

In the present study, the objective was to obtain a regression model that enables us to correlate a series of parameters with the age of a particular wine, with the aim of characterizing chemically how these parameters evolve with aging; with such a model, it would then be possible to guarantee the age of a wine from this series of objective variables.

This study presents our results with respect to the production of the model of wine aging. For this work, a total of 30 wines of known ages and kept under similar conditions have been utilized. The dates of production of these wines range from 1932 to 1999. The variables that have been studied are the routine analytical parameters, volatiles, short-chain organic acids, and phenolic compounds. The original wines of each sample analyzed differ with respect to their year of production, but the variety of grape and method of production employed are the same for all of the samples.

MATERIALS AND METHODS

The analytical determinations were made according to the methodology described below. The data corresponding to short-chain organic acids, volatiles, and phenolic compounds were obtained in the Department of Analytical Chemistry of the University of Cádiz, and the routine parameters were obtained using the official methods of analysis performed and provided by the producing Winery.

Determination of Short-Chain Organic Acids. This was performed by direct injection in a liquid chromatograph consisting of two LKB model 2150 pumps and an oven for 2155 columns (Pharmacia, Sweden), a 717 automatic injector (Waters, Milford, MA), and a Conductomonitor III conductivity detector (Milton Roy, LDC, FL), employing the Millenium 2.0 chromatographic control software (Waters, Milford, MA), following the method developed by Guillén et al. (*14*). Briefly, 50 mL of previously filtered sample (filter pore size of 0.45 μm) was injected. The separation was performed using an ION-300 ion-exclusion column (300 × 4.6 mm, from Interactions Chromatography, San José, CA). The temperature of the oven was set at 60 °C. The mobile phase employed was 2.5 mM trifluoroacetic acid (TFA) with a flow of 0.4 mL/min. To increase the sensitivity of the method, a solution of TFA (2.5 mM) and bis-tris (0.1 mM) buffer and AEDT was added to the outlet of the chromatographic column, employing for this a second pump using the same flow rate (0.4 mL/min).

Determination of Volatiles. The determination of volatiles was performed by the EU official reference method (*17*). The samples were submitted to distillation for cleaning and elimination of the heavy residues. The internal standard used was 4-methyl-2-pentanol, and 1 μL of the distillate was injected in a Hewlett−Packard 5890 series II gas chromatograph fitted with a DBWax capillary column (J&W Scientific, Folsom, CA) of 60 × 0.25 mm and 0.25 μm thickness and FID detector. The gas carrier was He, with a flow rate of 1 mL/min; the temperature of the injector was 200 °C and that of the detector was 250 °C. The injection mode was splitless, for 1.5 min. The temperature program of the oven began at 45 °C held for 20 min, increasing by 10 °C/min up to 95 °C, held for 1 min, then by 2 °C/min up to 130 °C, held for 1 min, then by 10 °C/min up to 210 °C, and held for 20 min.

For the quantification, the internal standard method with calibrations of each of the reference standards was utilized. The solutions of reference standards were prepared in distilled water containing 15% (v/v) of ethanol.

Determination of Phenolic Compounds. The determination of phenolic compounds was performed following the method developed by Guillén et al. (*18*). Briefly, the samples were injected at a volume of 80 μL, over a LiChrospher RP-18 column (Merck, Darmstadt, Germany). Two model 510 pumps, a model 717 injector, a model 996 PDA detector, and a 470 fluorescence detector (Waters, Milford, MA) were employed. The solvents employed were A (5:2:93, methanol/acetic acid/water) and B (90:2:8, methanol/acetic acid/water), with the elution being performed on a gradient (time, A%, B%: 0/100/0, 15/85/15, 50/50/50), employing a convex curve for the changes of composition of the eluent.

Statistical Techniques. The statistical techniques used to obtain regression models were multiple linear regression (MLR) and partial least squares (PLS). Two statistical packages were used: the UnScrambler version 7.5 (CAMO ASA, Norway) and STATGRAPHICS*Plus 5.1 Professional Edition (Manugistics, Inc., Rockville, MD).

Samples. The samples studied consisted of two groups. The first group comprised 30 samples of vintage Sherry wine, each produced from the individual harvest of a known year from 1930 to 1999, all made from the Palomino fino grape and all aged in oak barrels. Another group comprised 5 samples, also of vintage wines, but whose ages were unknown; however, they had been produced and aged in the same way as the first group. The samples and the information on their age were provided by the company Williams and Humbert Wineries, which keeps a special bodega for these wines.

RESULTS AND DISCUSSION

To conduct this study, the following 4 main groups of variables have been analyzed: short-chain organic acids, higher alcohols, phenolic compounds, and the routine analytical parameters, making a total of 34 variables. Some of these, *a priori*, could be correlated with the physicochemical aging that the wines undergo, while others would be supplied by the wood of the barrels in which they are aged.

The variables chosen correspond to parameters measured in all of the samples analyzed. In some of the vintages, certain variables were found below the limits of quantification of the methods employed, and for this reason, these have not been included in the regression models.

To check if there are some particular variables that could be correlated, to some degree, with the age of the wine, a

Table 1. Descriptive Statistic and Correlation Coefficients versus Age of the Variables Studied

variable	mean	SD	max	min	squared correlation coefficients of the variables studied versus age
citric acid (g/L)	0.59	0.589	2.14	0.05	0.4963
tartaric acid (g/L)	1.40	0.845	4.50	0.50	0.6606
malic acid (g/L)	0.25	0.209	0.94	0.04	0.0594
succinic acid (g/L)	0.60	0.414	2.29	0.21	0.5618
lactic acid (g/L)	1.87	1.556	7.23	0.16	0.6685
formic acid (g/L)	0.38	0.309	1.40	0.04	0.4951
acetic acid (g/L)	1.62	0.663	3.23	0.23	0.7944
escopoletin (mg/L)	0.39	0.327	1.34	0.00	0.7948
7-methylumbelliferone (mg/L)	0.26	0.345	2.08	0.01	0.3211
caftaric acid (mg/L)	11.49	21.781	80.44	0.17	0.4202
caffeic acid (mg/L)	2.74	8.112	45.36	0.00	0.1708
ferulic acid (mg/L)	3.01	8.331	43.92	0.09	0.0098
syringaldehyde (mg/L)	8.30	12.828	69.36	0.80	0.5111
vanillin (mg/L)	2.99	7.775	42.87	0.05	0.5588
5-hydroxymethylfuraldehyde (mg/L)	75.54	70.062	359.36	5.14	0.2012
furfural (mg/L)	52.38	51.648	246.49	4.03	0.5361
ethanol (% v/v)	23.25	1.768	25.90	19.10	0.6475
density (g/mL)	0.99	0.005	1.00	0.98	0.5108
pH	3.19	0.090	3.35	2.96	0.1035
total acidity (g/L tartaric acid)	8.68	2.370	14.25	4.80	0.8832
SO_2 (mg/L)	11.37	2.830	20.00	8.00	0.1034
volatile acidity (g/L tacetic acid)	1.66	0.549	2.85	0.65	0.8608
sugars (g/L)	7.52	3.393	16.50	1.80	0.0606
calcium (mg/L)	53.92	39.025	128.00	6.00	0.8297
acetaldehyde (mg/L)	148.43	60.240	260.00	43.00	0.2715
ethyl acetate (mg/L)	447.43	206.065	902.00	17.00	0.4150
n-propanol (mg/L)	77.67	57.694	324.00	4.00	0.6282
isobutanol (mg/L)	73.20	42.898	213.00	5.00	0.4182
n-butanol (mg/L)	8.50	5.935	32.00	1.00	0.0129
isoamyl alcohol (mg/L)	264.83	148.213	829.00	102.00	0.4998
acetoin (mg/L)	155.73	154.186	629.00	2.00	0.2836
ethyl lactate (mg/L)	344.77	436.658	2388.00	5.00	0.3120
2,3-butanediol (mg/L)	123.20	350.882	1899.00	1.00	0.2550
2-phenylethanol (mg/L)	69.50	63.377	288.00	7.00	0.0944

correlation study was made of individual variables; the results from this study are given in **Table 1**.

As can be seen, there are many variables that are positively correlated, with age, with values of r above 0.6. Among these are variables such as acetic acid and other related ones such as the volatile acidity and the total acidity that should be expected to increase with age because of oxidative processes of the ethanol. Another group of variables that also show positive correlation comprises vanillin, syringaldehyde, escopoletine, 7-methylumbelliferone, furfural, etc.; these are mostly extracted from the casks and logically increase in line with the time that the wine spends contained in the cask. An interesting finding is the behavior of calcium and tartaric acid, whose levels fall with time and which also have high correlation coefficients (-0.9109 and -0.8128, respectively); this behavior may be explained by a phenomenon of precipitation of tartrates. However, in general, there is no variable that, taken alone, could be used to correlate the age of the wine with the evolution of the variable.

Having performed this exploratory analysis, we studied the possibility of finding useful regression models by means of two statistical techniques.

PLS. The method of regression by PLS has been used extensively in chemometrics, where they have found a wide field of application. The PLS algorithm is based on a bilinear model, where the information contained in the X data matrix is projected over a small number of "latent" variables known as PLS components. The Y data matrix is actively used for estimating the "latent" variables to ensure that the first components of these are the most relevant for predicting the Y variables. The interpretation of the relationships between the X and Y data is simplified to the relationships between the smaller number of PLS components.

To apply the regression model, all of the variables of the samples from the years between 1935 and 1999 were processed; the samples from 1930 and 1932 were discarded because the set of data for these was incomplete. To attach a weighting to each variable, the data obtained were divided by the standard deviation of each series and later processed by means of the PLS1 algorithm of the Unscrambler program, utilizing the method of "leverage correction" for the validation.

The results obtained are shown in **Figures 1** and **2**. The regression model behaves fairly well in the range of years explored, giving several regression coefficients of 0.9951 and a slope between the calculated age and the measured age of practically 1 (0.9854) for the model with 4 principal components, with root-mean-square error of prediction for each PC of 5.82, 3.90, 3.06, and 2.08, respectively. This slope is even better in the case of utilizing 6 components (0.9902). When more PCs are utilized in the model, the effect is to introduce noise, as is demonstrated when the variance explained for PC7 and successive PCs is studied, in which cases the noise increases. **Figure 3** shows the contribution of each variable to PC1. This confirms the behavior that was already reflected in the exploratory study, in which the notable findings are the negative contributions of tartaric acid and calcium, probably because of a precipitation mechanism, the positive contributions of the acids related to oxidative aging and acetic and formic acids, and the total and volatile acidity, together with the positive contributions of phenolic compounds related to extraction from the wood (escopoletin, 7-methylumbelliferone, and vanillin).

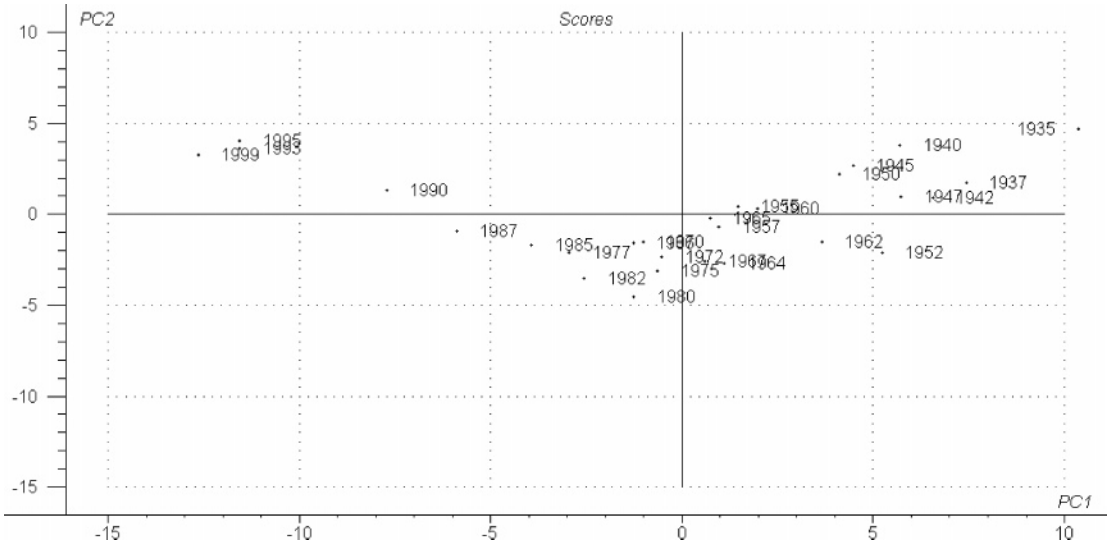

Figure 1. PC1 versus PC2 scores obtained in the calibration model using PLS.

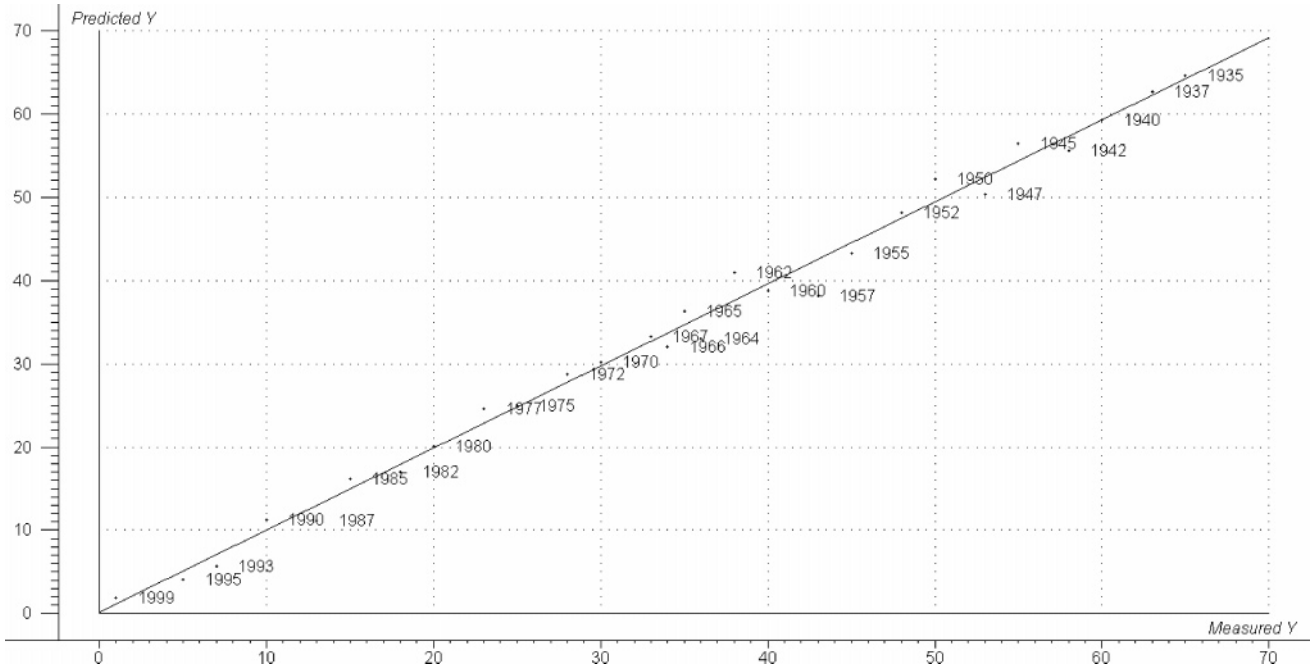

Figure 2. Regression line drawn against the prediction obtained in the calibration model using PLS.

With the object of checking the success of the method, the same set of samples was processed using the regression model previously obtained, and this gave a mean deviation of the predicted values of 1.6 years. The reliability of the model was thus demonstrated, because an age prediction range of less than 3 years is obtained and the largest errors occur in the predictions for the youngest wines. This result may be considered logical because it is at the extreme values where the model would theoretically have the largest errors; furthermore, it is in the youngest wines where the components related to the wood would present more variability, bearing in mind that the natural behavior of an extraction kinetic should be to follow a hyperbolic curve.

As an external method of checking, another model was constructed with all of the samples available except those corresponding to the years 1942, 1952, 1962, 1972, 1982, and 1993, with the aim of subsequently classifying these particular samples according to this model. The result obtained in this case was a correlation coefficient of 0.9923. The deviation of the prediction was found to be lower than ±3.0 years for all samples utilized for the validation. Moreover, the predicted age was within 10% for those samples presenting ages of more than 20 years (**Table 2**).

Last, the model obtained by including all of the samples available was later utilized to determine the ages of the second set of samples of vintage wines, of ages previously unknown to the researchers. The results obtained for this set of samples are presented in **Table 3**. Using the method employed, it can be determined if the prediction is reliable or not with respect to the separation or degree of difference between the actual samples to be evaluated and the samples employed for performing the regression. Specifically, among the "problem" samples analyzed, the error obtained for the solerae sample (50%) stands out: in this particular case, the sample is a wine with a very high content of sugars (glucose and fructose) as the result of being blended with sweet wine of the Pedro Ximénez variety. Because none of the samples employed for constructing the model presented similar characteristics, the prediction error for this wine turned

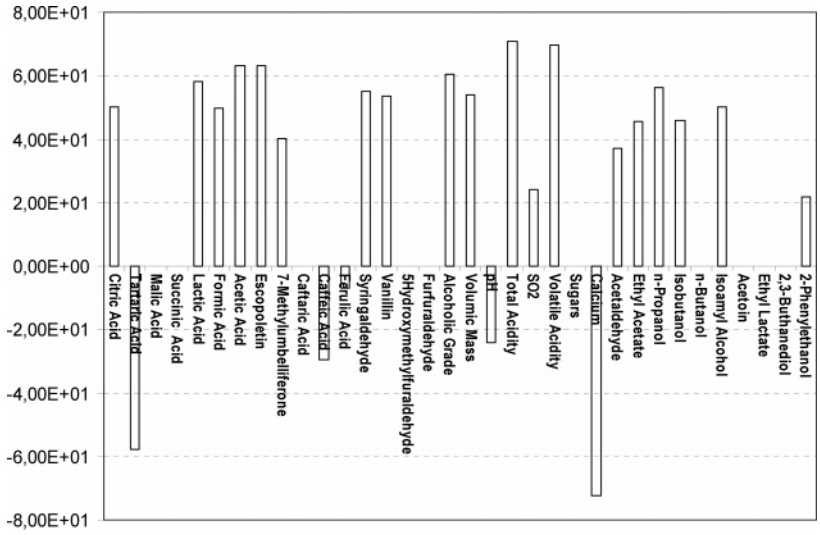

Figure 3. Contribution of the individual variables to the principal component of the regression model obtained using PLS.

Table 2. Prediction Obtained for the Samples Utilized for the Validation of PLS Model

sample	age	predicted age	deviation
1935	65.000	67.289	±2.183
1937	63.000	56.871	±2.054
1940	60.000	59.213	±1.843
1945	55.000	54.388	±1.547
1947	53.000	54.082	±1.830
1950	50.000	52.115	±1.590
1955	45.000	43.930	±1.351
1957	43.000	35.827	±1.384
1960	40.000	41.763	±1.838
1964	36.000	34.933	±1.520
1965	35.000	37.478	±1.442
1966	34.000	29.880	±1.521
1967	33.000	33.215	±1.351
1970	30.000	29.524	±1.668
1975	25.000	28.240	±1.617
1977	23.000	23.266	±2.481
1980	20.000	24.389	±1.971
1985	15.000	16.083	±1.755
1987	13.000	12.849	±1.992
1990	10.000	15.840	±1.785
1995	5.000	7.761	±2.423
1999	1.000	9.143	±2.846

Table 3. Predicted Age for the Unknown Samples Obtained by Means of the Regression Models Obtained by PLS and MLR

	PLS		MLR	
sample	age prediction (years old)	deviation	age prediction (years old)	deviation
clotilde	20.249	±3.233	23.340	±6.880
cristeta	31.439	±2.627	30.390	±4.005
lajulia	30.953	±5.835	38.700	±10.383
olorosodi	30.435	±3.897	33.095	±2.207
solerae	22.380	±11.425	16.606	±10.506

out to be especially high; it can therefore be concluded that, because the wine was not fitted to the model, its age could not be calculated by this method.

MLR. Before seeking the regression model, a study of normality was conducted using the Kolmogorov−Smirnov test for a 95% level of significance; from this, it was found that the following variables did not have a normal distribution: formic acid, 7-methylumbelliferone, caftaric acid, caffeic acid, ferulic acid, furfural, acetoin, and 2,3-butanediol. Subsequently,

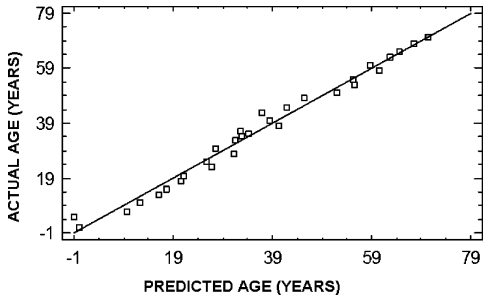

Figure 4. Regression line drawn against the prediction obtained in the calibration model using MLR.

the normality of the logarithmic function of these variables was studied, and it was found that, after this transformation, all of the variables were normal, apart from caffeic acid and 7-methylumbelliferone; it was therefore decided not to use these two variables in the subsequent studies.

Subsequently, a study of reduction of variables was carried out, and a model was obtained with 6 independent variables that explain 98.23% of the variability in age with an r^2 of 0.9777, a standard deviation of residuals of 2.9877, and a mean absolute error of 2.1674. The equation of the fitted model is

$$\text{age} = 10.7868 - 2.8454\log[\text{caftaric acid}] - 5.2819[\text{tartaric acid}] + 5.64782[\text{total acidity}] + 5.38772[\text{escopoletin}] - 4.30171[n\text{-butanol}] + 7.3217[\text{ethyl lactate}]$$

The function obtained is consistent with the oxidative aging process to which the wines studied have been subjected (*19*). As can be seen, the function relates the age to the following factors: (1) an increase of the total acidity and of the ethyl esters, which is a normal evolution in an oxidative aging process in a medium enriched in alcohol; (2) an increase of escopoletin, a compound extracted from the wood; (3) a decrease of caftaric acid, an ester of caffeic and tartaric acids that tends to hydrolyze over time; (4) a decrease of tartaric acid by precipitation of the tartrates; and (5) a decrease of *n*-butanol, a compound that gradually disappears by esterification.

Figure 4 shows the graph of predicted against observed age, in which the success of the model can be appreciated. When the model is applied to the set of samples, it is found that the mean deviation of the predicted values is 3.5 years.

Finally and as was done with the model obtained by PLS, the model obtained by MLR was applied to determine the age of the set of samples of previously unknown age. The results are given in **Table 3**. As can be observed when the results are compared with the prediction made using the PLS model, although the results are appreciably different, the order of ages predicted is similar in both cases.

It can be concluded that PLS and MLR, the statistical methods of regression used, utilizing the normal routine analytical parameters, polyphenols, organic acids, and phenolic compounds as predictive variables, can be used to determine the age of a vintage Sherry wine.

The model obtained by the utilization of PLS provides a more accurate prediction than the model obtained by MLR, although the latter requires fewer variables to obtain an acceptable regression model.

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LITERATURE CITED

(1) Singleton, V. L. Maturation of wines and spirits—Comparisons, facts, and hypotheses. *Am. J. Enol. Vitic.* **1995**, *46*, 98−115.

(2) Perez-Coello, M. S.; Sanz, J.; Cabezudo, M. D. Determination of volatile compounds in hydroalcoholic extracts of French and American oak weed. *Am. J. Enol. Vitic.* **1999**, *50*, 162−165.

(3) Martínez, R. G.; Serrana, H. L. G.; Mir, M. V.; Granados, J. Q.; Martínez, M. C. L. Influence of wood heat treatment, temperature, and maceration time on vanillin, syringaldehyde, and gallic acid contents in oak wood and wine spirit mixtures. *Am. J. Enol. Vitic.* **1996**, *47*, 441−446.

(4) Spilman, P. J.; Pollnitz, A. P.; Liacopoulos, D.; Skouroumounis, G. K.; Sefton, M. A. Accumulation of vanillin during barrel-aging of white, red, and model wines. *J. Agric. Food Chem.* **1997**, *45*, 2584−2589.

(5) Towey, J. P.; Waterhouse, A. L. The extraction of volatile compounds from French and American oak barrels in Chardonnay during three successive vintages. *Am. J. Enol. Vitic.* **1996**, *47*, 163−172.

(6) Galletti, G. C.; Carnacini, A.; Boccini, P.; Antonelli, A.; Chemical-composition of wood casks for wine aging as determined by pyrolysis/GC/MS. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 1331−1334.

(7) Fabios, M.; López-Toledano, A.; Mayén, M.; Mérida, J.; Medina, M. Phenolic compounds and browning in Sherry wines subjected to oxidative and biological aging. *J. Agric. Food Chem.* **2000**, *48*, 2155−2519.

(8) Puech, J. L.; Feuillat, F.; Mosedale, J. R. The tannins of oak heartwood: Structure, properties, and their influence on wine flavor. *Am. J. Enol. Vitic.* **1999**, *50*, 469−478.

(9) Canas, S.; Leandro, M. C.; Spranger, M. I.; Belchior, A. P. Low molecular weight organic compounds of chestnut wood (*Castanea sativa* L.) and corresponding aged brandies. *J. Agr. Food Chem.* **1999**, *47*, 5023−5030.

(10) Cutzach, I.; Chatonnet, P.; Dubourdieu, D. Study of the formation mechanisms of some volatile compounds during the aging of sweet fortified wines. *J. Agric. Food Chem.* **1999**, *47*, 2837−2846.

(11) Granados, J. W.; Mir, M. V.; Serrana, H. L. G.; Martinez, M. C. L. The influence of added caramel on furanic aldehyde content of matured brandies, *Food Chem.* **1996**, *56*, 415−419.

(12) Martin, G. J.; Nicol, L.; Naulet, N.; Martin, M. L. New isotopic criteria for the short-term dating of brandies and spirits. *J. Sci. Food Agr.* **1998**, *77*, 153−160.

(13) Ortiz, M. C.; Sarabia, L. A.; Symington, C.; Santamaria, F.; Inigueze, M. Analysis of aging and typification of vintage ports by partial least squares and soft independent modelling class analogy. *Analyst*, **1996**, *121*, 1009−1013.

(14) Guillén, D. A.; Barroso, C. G.; Zorro, L.; Carrascal, V.; Pérez-Bustamante, J. A. Organic acids analysis in "Brandy de Jerez" ion-exclusion chromatography, "post-column" buffering, and conductometric detection. *Analusis* **1998**, *26*, 186−189.

(15) Watts, V. A.; Butzke, C. E.; Boulton, R. B. Study of aged cognac using solid-phase microextraction and partial least-squares regression. *J. Agric. Food Chem.* **2003**, *51*, 7738−7742.

(16) Perez-Coello, M. S.; Martín-Álvarez, P. J.; Cabezudo, M. D. Prediction of the storage time in bottles of Spanish white wines using multivariate statistical analysis. *Z. Lebensm.-Unters. Forsch. A* **1999**, *208*, 408−412.

(17) Reglamento (CE) no 2870/2000 de la Comisión de 19 de Diciembre de 2000. Diario Oficial de las Comunidades Europeas de 29-12-2000, L-333/20−46.

(18) Guillen, D. A.; Barroso, C. G.; Perez-Bustamante, J. A. Selection of column and gradient for the separation of polyphenols in Sherry wine by HPLC, incorporating internal standards. *J. Chromatogr.* **1996**, *724*, 117−124.

(19) Flanzy, C. *Enología: Fundamentos Científicos y Tecnológico*, A. Madrid Vicente, Ediciones, y Ediciones Mundi-Prensa: Madrid, Spain, 2000.

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