SHERRY WINES. COMPOSITION AND ANALYSIS

by

Medina, M., Moreno, J., Merida, J., Mayen M., Zea, L. and Moyano, L.

Department of Agricultural Chemistry. Faculty of Sciences. University of Cordoba
Edificio C-3. Campus de Rabanales. 14014. Cordoba. Spain
E-mail: **vitenol@uco.es** Web site: **http://www.uco.es/grupos/vitenol/index.htm**

Most Sherry wines are produced in two southern regions of the Spain, Jerez and Montilla-Moriles, where the grape varieties *Palomino Fino* and *Pedro Ximenez*, respectively, are preferentially grown. These grapes are used to obtain so-called fino, oloroso and amontillado wines, which are typical three types of these wines. The three are obtained starting from a same wine base but subjected to different aging conditions. Fino wines possess a very light yellow color and an almond flavor with pungent notes. Like some Italian and French like-sherry wines, they are obtained by biological aging under the action of flor yeasts growing on the wine surface. This aging procedure involves a complex series of wine transfers that leads to a mixture of different vintages in the same cask. Oloroso wines are obtained by oxidative aging, after fortification with ethanol in order to prevent growth of flor yeasts. They possess a very dark color that results from the oxidation of phenolic compounds, and a flavor with distinct notes of oak and walnut. Amontillado wines are produced by using the previous two aging procedures in succession (biological aging first and oxidative aging then). These wines are highly appreciated, possess a color in between those of fine and oloroso wines, but closer to the latter, and a flavor with hazelnut notes that is the most complex among the three.

MUSTS AND WINES. GENERAL COMPOSITION

The prevailing climate of the sherry-making regions of southern Spain determines to a great extent the general composition of the musts and wines they produce, and also some winemaking techniques. In summer, temperatures above 35 ºC, or even above 40 ºC in areas distant from the Mediterranean coast, are usual during the grape ripening period. By exception, a milder climate can be found in zones such as Sanlucar de Barrameda, at the sea side, where is produced a wine similar to fino type (called Manzanilla), but with distinctive sensorial characteristics. Under these climatic conditions, grapes accumulate large amounts of reducing sugars, which results in concentrations above 200 g/L in must (specific gravity 1.094 g/mL) or even higher than 270 g/L (specific gravity 1.113 g/mL) in the warmer areas. As a result, the base wines obtained after alcoholic fermentation show high ethanol contents and are classified according to their ability for producing the different types of sherry wines. Wines to be aged biologically are fortified up to 15% v/v ethanol content, if necessary, whereas those destined to the production of oloroso wines are fortified to 17-18% v/v.

The climatic conditions also result in musts with low acidity (3-4.5 g/L as tartaric acid) that is usually increased by addition of tartaric acid, although winemakers in some areas continue to use gypsum for this purpose. The musts are also supplied with SO_2 at concentrations around 100 mg/L.

The special features of the process by which flor yeasts produce fino wine have aroused much interest among researchers. The yeast types most frequently used for this purpose are *Saccharomyces cerevisiae* races *beticus*, *cheresiensis* and *montuliensis* in the Jerez region, and races *capensis* and *bayanus* in the Montilla-Moriles region. Qualitatively, these yeasts develop an aerobic metabolism consuming ethanol (1-1.5% v/v) and glycerol (decreasing from 7-8 g/l to below 0.5 g/L), in addition to some acids such as acetic (the concentration of which as volatile acidity falls from 0.4 to 0.04 g/L) and lactic, which are converted to acetaldehyde and other byproducts. Quantitatively, however, changes during the biological aging process depend on the distribution of the yeast population and on the stability of the film they form; this results in some differences among fino wines produced in different zones. On the other hand, the development of flor yeasts is essentially influenced by the ethanol content in the wine (around 15% v/v) and the temperature during aging (below 22.5 ºC). Move away from these conditions (e.g. higher temperatures) deteriorates the flor film and retards the aging process.

In the absence of flor yeasts, oloroso wines consume no glycerol, which remains at levels of 6.5-8 g/L during oxidative aging. On the other hand, their volatile acidity increases during aging (up to 0.68 g/L as acetic acid), because of the oxidation of ethanol and acetaldehyde. Amontillado wines exhibit a intermediate behavior between those of the previous two as a result of the mixed aging procedure used.

Obtaining quality sherry wines of the three types entails very long aging times: at least 4-5 years for fino wines and more than twice longer for amontillado wines. In order to shorten the process, some authors recommend the use of various procedures to accelerate biological aging of the wine. Such procedures are based in an increase in the population densities of flor yeasts, which can be obtained by using containers with an increased surface-to-volume ratio or controlled aerations of the wine while aging. Oloroso wines have also been subjected to accelerated aging procedures involving higher temperatures or maceration with oak wood shavings.

VOLATILE COMPOUNDS AND FLAVOR

Musts and wines

Palomino Fino and *Pedro Ximenez*, the two grape varieties preferentially used to obtain Sherry wines in the Jerez and Montilla-Moriles regions, are scarcely aromatic with an overall free terpenes content in the musts of the 0.27-0.37 mg/L for the last variety. In order to improve the sensory profile of the must, cold maceration with grape skin at 10 ºC for 24 hours has been found to increase the terpenes content by a factor of 4.5, however these results probably do not offset the cost of the operations involved.

Traditionally, the musts are fermented with wild yeasts, the population consisting preferentially of various *Saccharomyces cerevisiae* races. The content in higher alcohols (mainly isobutanol, isoamyl alcohols and phenethyl alcohol) at the end of fermentation ranges from 207 to 405 mg/L. Relative to other types of white wines the ester fraction is less concentrated, as a result the wine possesses a strong, hard sensory profile prior to aging. This is also a result of a high fermentation temperature (frequently above 25 ºC), which favors the formation of higher alcohols. Pure and mixed cultures of the yeasts have been tested with a view to softening the sensory profile of the base wine. In this sense, some authors have studied the enzymatic activity of acetyl transferase and esterase in pure cultures of the fermentation yeasts in order to determine the contribution of specific yeasts races involved in the alcoholic fermentation process to the flavor of the base wine. However, the need to ferment large amounts of sugars, and as a consequence a high tolerance to ethanol, makes replacing the wild yeasts very difficult.

Wine Aging

Most of the analytical and sensory differences among Sherry wines result from differences in the aging procedures to which the base wines are subjected. On the one hand, the biological aging process that yields fino wine is effected by flor yeasts, which use some compounds in the base wine as carbon sources, thereby altering its composition to a variable extent depending on the duration of the process. On the other hand, the oxidative aging process that produces oloroso wine allows for no biological transformation, so the changes involved should be preferentially ascribed to evaporation, chemical oxidation and extraction from constituents of the wood casks. Because amontillado wine is obtained by a combination of both types of aging procedure, its analytical properties are inherited to a variable extent, even through its sensory profile is specific of this wine type.

More than 300 different compounds have so far been identified in Sherry wines obtained by biological aging. Only a small fraction, however, can be specific to them, corresponding the most of the analytical differences observed to changes in the concentrations of compounds also present in other types of white wines. Worth special note here are the contents in acetaldehyde and derivatives such as 1,1-diethoxyethane and acetoin. The concentrations of these compounds increase during biological aging as a result of the aerobic metabolism of flor yeasts consuming the ethanol of the wine. Their concentrations in commercially available wines range between 400-500 mg/L for acetaldehyde, 40-75 mg/L for 1,1-diethoxyethane and 8-19 mg/L for acetoin, depending on the duration of the aging process. Acetaldehyde is thus used as a measure of wine maturity, it being largely responsible for the typical pungent flavor of fino wines. Some lactones and their oxygen-derivatives also impart differential notes to the flavor of wines obtained by biological aging. In fact, despite their low concentrations, some lactones such as sotolone (0.036-0.143 mg/L), γ-butyrolactone (27-54 mg/L) and pantolactone (3-8.5 mg/L) impart a caramel-like odor to these wines and increase their concentration during biological aging. Particularly, the former is considered as an important contributor to the flavor of fino wines, introducing nut-curry notes. One other distinctive feature of the biological aging process is the decrease in volatile acidity resulting largely from the consumption of acetic acid by flor yeasts, which reduces its typical odor and flavor.

Changes in other aroma compounds are not so clear as those in the above-mentioned compounds. Although some authors have reported a decrease in the contents of major higher alcohols, others have found slightly increased or constant contents. These contradictory results are probably a consequence of differences in the experimental conditions used, particularly as regards the distribution of the flor yeast population and the aging temperature. In relation to the ester changes during aging can also be observed contradictory results, although increased contents in ethyl lactate and diethyl succinate, and decreased contents in ethyl, isoamyl, isobutyl and phenethyl acetates, appear to be the norm. Some authors have found flor yeasts to synthesize small amounts of terpenes such as linalool, α-terpineol and z-nerolidol.

The aroma fraction of oloroso and amontillado wines is mainly influenced by a concentrating effect during their lengthy aging; as a result, the contents in major higher alcohols and esters increase with increasing wine age. Also, chemical esterification is favored by a high ethanol content in the wine, so the concentrations of esters such as ethyl acetate, ethyl lactate and diethyl succinate increase during aging.

PHENOLIC COMPOUNDS AND COLOR

Color is the most obvious distinctive feature of Sherry wines for the consumer. Thus, fino wines, which are obtained by biological aging, exhibit a very pale yellow color , whereas amontillado and, especially, oloroso wines, possess a dark color .

Musts and wines

More than 20 phenolic compounds in monomeric and simple oligomeric forms have been identified in the base wines prior to aging. Although their concentrations depend markedly on the particular climatic conditions of each year and on the grape ripening status, flavan-3-ol derivatives invariably exhibit the highest concentrations of all (100-120 mg/L, most of which is contributed by catechin and epicatechin). The concentrations of hydroxycinnamic acids range from 1 to 5 mg/L and those of their esters from 45 to 75 mg/L, in which t-caftaric acid is the best represented. Gallic acid exhibits the highest contents among hydroxybenzoic acids (the overall concentration of which ranges from 15 to 25 mg/L). Flavonols and coumarins are also present, at concentrations of 10-20 and about 50 mg/L, respectively.

Fino wine is a delicate product because its trends to browning after bottling. This alters not only its color but also its sensory properties. Thus, freshly marketed fino wine has an absorbance at 420 nm of 0.100-0.120 au and reaching 0.170-180 au, it is normally discarded. Depending on the particularly production technique used, this absorbance threshold is reached within about one year after bottling. This has promoted the development of improved production techniques to better balance supply and demand in order to avoid overstocking. Because brown pigments in the wine are formed by oxidation of phenolic compounds, winemaking techniques such as must hyperoxidation have been used to decrease the contents in these compounds and increasing the resistance of the resulting wines to browning. However, one should bear in mind the complexity of the aging process, by which a given cask contain mixed wines from different vintages. Thereby, reliable conclusions on this point can only be reached from a "solera and criadera system" exclusively using hyperoxidized wines from various vintages, it requiring a long term research. Also for improve the resistance to browning, traditional habits such as the addition of SO_2 to grapes during the harvest period have been suppressed because they result in increased extraction of phenolic compounds from grape skin.

Wine aging

Because of their differential aging processes, the three types of Sherry wine differ in their contents in phenolic compounds. Thus, flavan-3-ol derivatives, predominate in fino wines (with concentrations of 60-80 mg/L), followed by hydroxycinnamic esters (15-25 mg/L), hydroxybenzoic acids (15-30 mg/L), flavonols (5-10 mg/L) and hydroxycinnamic acids (1.5-2.5 mg/L). The contents in vanillic and ferulic acids, catechin, epicatechin and procyanidin B2 and B4, have been found to decrease during biological aging, while those of syringic acid and procyanidin B1 appear to increase during the process. It should be pointed out that this type of wine does not brown under flor yeasts, preserving its pale color with slight oscillations for years. This has traditionally been ascribed to the flor yeasts that grow on its surface making difficult the diffusion of atmospheric oxygen across the flor film and protecting wine from it. In addition, flor yeasts consume dissolved oxygen in the wine to maintain their aerobic metabolism, thereby preventing the oxidation of phenolic compounds. However, the only contribution of this protective effect to color stability in the wine subjected to biological aging has been partly questioned by some authors who believe that the wine is partially oxygenated over the years as a result of two actions. On the one hand older wine is mixed with younger wine three or four times a year, which introduces some oxygen during the transfer operations. On the other hand the flor film fails in some year seasons because of its strong dependence of the temperature. These veil lacks expose the wine surface and facilitate the access of atmospheric oxygen. In fact, the absorbance values at 420 nm measured at the end of summer are normally higher than those recorded in late spring and autumn. Thereby, in addition to the above-mentioned protective effect of the flor film, some authors think that yeasts may be able to retain brown polymers formed by oxidation of phenols.

Oloroso wines are considerably darker than fino wines as a result of their oxidative aging. In fact, their corrected for dilution absorbance values at 420 nm range from 1.30 to 1.60 au. The phenolic contents of these wines exceed those in fino wines, with levels in between of 35-45 mg/L for hydroxybenzoic acids, 5-20 mg/L for hydroxycinnamic acids, 20-25 mg/L for hydroxycinnamic esters and 100-130 mg/L for flavanes. These increased contents can be ascribed to two factors with especially marked effects on this type of aging process. Thus, the higher ethanol contents of oloroso wines facilitate the extraction of phenols from the wood casks. Also, oxidative aging usually takes place at a higher temperature than does biological aging, which results in volume loses in the aging wine, with the subsequent concentrating effect on the soluble compounds.

Amontillado wines show intermediate levels in between the previous two because of the combined aging process used in their production, so their corrected absorbance at 420 nm range from 0.950 to 1.100 au. However, in general, their phenol contents are similar to those of oloroso wines, with values between 45-75 mg/L for hydroxybenzoic acids, 5-15 mg/L for hydroxycinnamic acids and 125-160 mg /L for flavanes.

OTHER COMPOUNDS

Amino acids are important compounds because their use by the flor yeast as nitrogen source. L-proline is the predominant compound of this fraction in the wines base accounting for about 60% of total nitrogen, with a concentration in between of 4.5-7.5 mmol/L. Other abundant amino acids are L-tryptophan (8%), L-phenylalanine

(7.5%), L-cysteine (6%) and L-threonine (3%). L-proline is the most heavily used nitrogen containing compound and the principal source of nitrogen for the flor yeast, thereby this compounds is consumed preferentially during biological aging. In the deficiency of L-proline, flor yeast use other amino acids such as L-glutamic acid, L-alanine, L-arginine and L-tryptophan. Oloroso wines show slightly increased contents in amino acids as a result of the above mentioned effect of volume concentration during the oxidative aging.

The most abundant polyalcohols quantified in sherry wines are inositol and erythrol, in variable levels depending on winemaking. No significant changes have been observed during aging because of the initial variability of wine base is greater than the contribution of the maturation processes. However, it should be pointed out a general trends to higher contents in these compounds for the oloroso and amontillado wines.

BIBLIOGRAPHY

Baron, R.; Mayen, M.; Merida, J. and Medina, M. Changes in phenolic compounds and browning during biological aging of Sherry type wine. 1997. *J. Agric. Food Chem.*, **45**, 5, 1682-1685

Casas Lucas, J. Descripción resumida de la técnica enológica de los vinos de Jérez. 1985. *III Jornadas Univ. Jerez*. Ed. Univ. Cadiz

Cortes, M.B.; Moreno, J.J.; Zea, L.; Moyano, L. and Medina, M. Response of the aroma fraction in sherry wines subjected to accelerated biological aging. 1999. *J. Agric. Food Chem.* , **47** (8): 3297-3302.

Domecq, P. Sherry: state of art on a very special fermentation product. 1989. *Proc. Int. Symp. Yeasts* (Issy XIII), pp. 15-35, Belgium

Fabios, M.; Lopez-Toledano, A.; Mayen, M.; Merida, J. and Medina, M. Phenolic compounds and browning in sherry wines subjected to oxidative and biological aging. 2000. *J. Agric. Food Chem.*, **48** (6): 2155-2159.

García-Barroso, C.; López Sánchez, L. Otero, J.C.; Cela-Torrijos, R. and Pérez-Bustamante, J.A. Studies on the browning of the fino sherry and its relation to polyphenolic compounds. 1989. *Z. Lebensm Unters Forsh*, **189**: 322-325.

Guichard, E.; Etievant, P.; Henry, R. and Mosandl, A. Enantiomeric ratios of pantolactone, solerone, 4-carboethoxy-4-hydroxy-butyrolactone and of sotolon, a flavor impact compound of flor-sherry and botrytized wines. 1992. *Z. Lebens. Unters. Forschung*, **195** (6): 540-544.

Ibeas, J.I.; Lozano, I.; Perdigones, F. and Jimenez, J. Effects of ethanol and temperature on the biological aging of sherry wines. 1997. *Am. J. Enol. Vitic.*, **48** (1): 71-74.

Martin, B.; Etievant, P.X.; Lequere, J.L. and Schlich, P. More clues about sensory impact of sotolon in some flor sherry wines. 1992.. *J. Agric. Food Chem*, **40** (3): 475-478.

Martinez, P.; Rodriguez, L.P. and Benitez, T. Evolution of flor yeast population during the biological aging of fino sherry wine. 1997. *Am. J. Enol. Vitic.*, **48** (2): 160-168.

Martinez, P.; Rodriguez, L.P. and Benitez, T. Velum formation by flor yeasts isolated from sherry wine. 1997. *Am. J. Enol. Vitic.*, **48** (1): 55-62.

Mauricio, J.C., Moreno, J. and Ortega, J.M In vitro specific activities of alcohol and aldehyde dehydrogenases from 2 flor yeasts during controlled wine aging. 1997. *J. Agric. Food Chem*, **45** (5): 1967-1971.

Mesa, J.J.; Infante, J.J.; Rebordinos, L. and Cantoral, J.M. Characterization of yeasts involved in the biological aging of sherry wines. 1999. *Food Sci. Technol.-Lebens.-Wissen. & Technol.*, **32** (2): 114-120.

Moyano, L., Moreno, J., Millan, C. and Medina, M. Flavour in Pedro Ximénez grape musts subjected to maceration processes. 1994. *Vitis*, **33**: 87-91.

Webb, A.D. and Noble, A.C. Aroma of sherry wines. 1976. *Biotech. and Bioeng*. XVIII. 939-1052.

KEYWORDS

Sherry wine
White wine
Wine Composition
Wine Color
Wine Flavor
Phenolic Compounds
Aroma Compounds
Biological aging
Oxidative aging
Flor Yeast
Fino wine
Oloroso wine
Amontillado wine