Variations of the Major Volatiles Through Aging of Sherry

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A study was made of the variations in concentration of the major volatile components of sherries during the various aging stages. These variations were found to be due to the biological or physical-chemical nature of the various aging processes used in the area. A series of enzymatic reactions take place in wine during biological aging caused by the metabolism of the yeast acting in the medium; these produce reductions in volatile acidity, alcohol grade, and concentration of acetic acid esters. Other compounds undergo concentration owing to physical-chemical effects. In wines whose aging is purely physical-chemical, the reaction most commonly observed is chemical oxidation of the compounds caused by the oxygen in the air. This is true for acetaldehyde, which gradually becomes acetic acid and is in turn esterified with the predominant ethanol. Furthermore, a noticeable concentration of other compounds is observed, due to selective penetration through the wood of the butts.

Many of a wine's organoleptic characteristics are conditioned by the volatile compounds it contains (18). Most of the olfactory qualities, for example, are stimulated by alcohol, esters, or aldehydes, and some qualities detected by taste originate from volatile compounds (*e.g.*, the characteristic flavor of acetic acid).

An attempt has recently been made to arrive at correlations from which a wine's quality can be established according to its content of certain compounds (8). The more volatile compounds have greater organoleptic impact; however, many factors affect quality and determine the quantities of volatile compounds in wines.

The quantities of volatile compounds in a wine are affected by factors ranging from vine type and cultivation practices to the fermentation and aging techniques used. Fermentation temperature and aging technique can be important factors.

The aging system used in sherry-making is unique (6). It differs from all other methods in that it is not static, but takes on dynamic qualities. Products at different stages of aging are mixed according to set sequences to obtain the final product. Furthermore, aging may be biological (Jerez Fino), physical-chemical (Jerez Oloroso), or may involve both types of aging successively (Jerez Amontillado) (3,10).

Because of these aging practices, the different types of wine in the area evolve differently during aging and hence contain varying concentrations of volatile compounds and differ clearly from wines of other areas.

With this in mind, a study was made of the variations in concentration of certain volatile compounds in sherry during aging. The study was based on a large number of samples of wine from standard industrial systems. The main causes of variations in concentration detected are given, and a comparison is made between biological and physical-chemical processes.

Materials and Methods

Studies in aging have been done on a number of enological parameters and their changes in a series of industrial processes in the Sherry area.

The aging processes ("solera systems") are used to make four main types of sherry, each quite different from the others: Fino, Manzanilla, Oloroso, and Amontillado. We have studied each type of wine separately.

Samples were taken from 12 solera systems for Fino, two for Manzanilla, four for Oloroso, and two for Amontillado. Each solera system was formed by 2500 oak butts (containing 600 L) and was divided into five stages (500 butts each) of aging called, in ascending order of age, "Sobretablas," "3rd Criadera," "2nd Criadera," "1st Criadera," and "Solera," respectively.

The time of aging in each stage in the solera systems has been estimated using a method described in the literature (10). The average aging time for each system is shown in Table 1. A good description of the characteristics and operation of industrial solera systems can be found in the works of Casas (3,4) and Pérez (10).

Table 1. Estimated average time for each aging stage (years) and type of wine studied.

Stage			Aging system			
No.	Denomination		Fino	Manzanilla	Oloroso	Amontillado
1	Sobretablas	(S/T)	1.00	1.00	-	*
	Añada (Ada)		-	-	4	-
2	3rd criadera	(3Cra)	1.75	1.75	6	6
3	2nd criadera	(2Cra)	2.50	2.50	8	8
4	1st criadera	(1Cra)	3.25	3.25	10	10
5	Solera (Sra)		4.00	4.00	12	12

* In the case of the Amontillado system, the first four years are equivalent to biological aging in a Fino system.

For each of the 20 aging systems studied, 50-mL samples of wine were taken from the center of each butt. For each system and stage of aging, samples from all 500 butts were blended in a 25-L tank. From these blends, 750-mL samples (one for each system and stage) were taken and stored at −20°C for later analysis. In order to compensate for climatic effects, the sampling process was carried out three times over a year.

Samples analysis: pH was measured with a digital pH meter, equipped with a combined electrode. Total acidity was determined by titration according to the method of the American Society of Enologists (1). Volatile acidity and alcohol grade were determined by the OIV standard volumetric method (9) and a Dujardin-Salleron-type ebulliometer (2), respectively. Density (D20/20) was measured using the pycnometric method (15). Acetalde-

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Table 2. Parameters for Fino-type wines studied according to aging stages.

Parameter	(Units)	Aging stage S/T	3Cra	2Cra	1Cra	Sra
Alcohol grade	(°GL)	16.0	15.4	15.1	14.8	14.6
TA	(g tartaric/L)	5.27	4.98	4.78	4.37	3.95
VA	(g tartaric/L)	0.39	0.38	0.30	0.24	0.21
pH		3.26	3.16	3.20	3.28	3.33
Density	(g/mL)	0.9874	0.9862	0.9859	0.9857	0.9852
Acetaldehyde	(mmol/L)	2.25	4.27	5.63	6.24	6.54
Methyl acetate	(mmol/L)	0.39	0.41	0.38	0.36	0.36
Ethyl acetate	(mmol/L)	0.83	0.89	0.81	0.70	0.66
Methanol	(mmol/L)	2.00	2.31	2.53	2.65	2.78
n-Propanol	(mmol/L)	0.57	0.70	0.83	0.93	0.98
n-Butanol	(mmol/L)	0.05	0.07	0.07	0.08	0.08
2-Butanol	(mmol/L)	-	-	-	-	-
i-Butanol	(mmol/L)	1.16	1.00	1.09	1.17	1.22
i-Amyl alcohols	(mmol/L)	2.73	2.37	2.55	2.76	2.92

hyde, methyl acetate, ethyl acetate, methanol, *n*-propanol, *n*-butanol, 2-butanol, *i*-butanol, and *i*-amyl alcohols were determined by gas chromatography (5).

Chromatographic analysis was performed on a Varian model 3700 gas chromatograph backed up by a Hewlett Packard 3390A recorder/integrator. The stainless steel chromatographic column was 2 m in length with 1.8 mm i.d. The stationary phase was Carbowax 1500 supported on Chromosorb 80-100 mesh. Analytical conditions were as follows: double F. I. D. detector; oven temperature, 90°C; injector temperature, 250°C; detector temperature, 200°C; carrier gas, nitrogen; flow rate, 30 mL/min; internal standard, 2-pentanol.

Results and Discussion

Tables 2, 3, 4, and 5 show the average values from the analyses carried out on samples taken in each solera system. Tables 2 and 3 show the results obtained for biologically aged wines and Tables 4 and 5 those for physically-chemically aged wines.

For a probability factor of 95%, the confidence limits of the average values obtained from the student's t statistical method were never above 5% of the average. The statistical treatment shows that there are no significant differences between solera systems of the same type.

Results are discussed on the basis of the differentiation between wines (biologically or physically-chemically aged).

Biological aging: When studying the tendencies towards variation in concentrations, it should be remembered that the criadera and solera stages are dynamic, while the initial sobretablas or añada stages are static. Thus, the composition of añada or sobretablas clearly reflects the characteristic of each specific vintage, whereas with the advance through the remaining stages of the system, the differences in character between the vintages become blurred and the effects of the aging system itself become clearer.

One of the most important changes in the wine's composition during biological aging is the reduction of total acidity. The major cause of this lies in the precipitation of potassium bitartrate during the long storage period (16), an effect enhanced in winter by the fall in temperature. Precipitation has been estimated at *ca* 1 g KHT/L over the entire aging period, a 20% reduction in acidity. At the same time, although to a lesser extent, loss of acidity is influenced by the considerable reduction in volatile acidity due to the consumption of acetic acid by the yeast in order to synthesize its cell compounds (fatty acids and proteins) along the various metabolic pathways available (12).

Reduction in alcohol grade throughout the processes is also explained by assimilation by the yeasts (in this

Table 3. Parameters for Manzanilla-type wines studied according to aging stages.

Parameter	(Units)	Aging stage S/T	3Cra	2Cra	1Cra	Sra
Alcohol grade	(°GL)	16.0	15.2	14.9	14.7	14.5
TA	(g tartaric/L)	5.27	4.94	4.65	4.54	4.24
VA	(g tartaric/L)	0.39	0.40	0.38	0.36	0.27
pH		3.26	3.16	3.19	3.29	3.32
Density	(g/mL)	0.9874	0.9860	0.9859	0.9858	0.9856
Acetaldehyde	(mmol/L)	2.25	3.34	4.02	4.63	5.27
Methyl acetate	(mmol/L)	0.39	0.59	0.58	0.57	0.55
Ethyl acetate	(mmol/L)	0.83	0.94	0.92	0.85	0.73
Methanol	(mmol/L)	2.00	2.62	2.75	2.84	2.87
n-Propanol	(mmol/L)	0.57	0.72	0.82	0.85	0.90
n-Butanol	(mmol/L)	0.05	0.05	0.05	0.05	0.07
2-Butanol	(mmol/L)	-	-	-	-	-
i-Butanol	(mmol/L)	1.16	1.00	1.09	1.15	1.23
i-Amyl alcohols	(mmol/L)	2.73	2.12	2.19	2.20	2.28

Table 4. Parameters for Oloroso-type wines studied according to aging stages.

Parameter	(Units)	Aging stage Ada	3Cra	2Cra	1Cra	Sra
Alcohol grade	(°GL)	18.2	18.9	19.1	19.4	19.6
TA	(g tartaric/L)	4.80	5.43	5.53	5.59	5.59
VA	(g tartaric/L)	0.69	0.90	1.03	1.15	1.15
pH		3.16	3.46	3.43	3.39	3.35
Density	(g/mL)	0.9841	0.9835	0.9840	0.9844	0.9848
Acetaldehyde	(mmol/L)	3.45	3.63	3.63	3.66	3.68
Methyl acetate	(mmol/L)	0.28	0.30	0.35	0.38	0.43
Ethyl acetate	(mmol/L)	1.91	2.37	2.50	2.85	3.18
Methanol	(mmol/L)	3.50	3.87	4.43	4.68	5.09
n-Propanol	(mmol/L)	0.72	0.77	0.87	0.92	1.03
n-Butanol	(mmol/L)	0.04	0.04	0.04	0.05	0.07
2-Butanol	(mmol/L)	-	-	-	-	-
i-Butanol	(mmol/L)	0.82	0.92	0.97	1.07	1.19
i-Amyl alcohols	(mmol/L)	2.04	2.75	2.89	2.95	2.98

case, ethanol) which, in the absence of sugars in the medium, become the main source of organic carbon. The ethanol consumption maintained during the processes is calculated, according to the data in Tables 2 and 3, at over 10 g/year/dm^2 active yeast surface. It should be stressed that the alcohol grades detected in the systems studied are slightly higher than normal because alcohol grade is adjusted periodically (sometimes after several years) to avoid excessive loss. For this reason, biological aging systems may show alcohol grade values up to 0.5° lower than those shown in the tables.

It must also be pointed out that prior to the first aging stages, alcohol grades are adjusted using distilled wine alcohol. Because of its origin, this alcohol (while containing practically no *i*-amyl alcohols) has high concentrations of acetaldehyde and other compounds, so the initial concentrations of these compounds are modified by the addition of the alcohol. This operation, frequently undertaken in the area (to a greater or lesser extent according to the type of wine involved) is one of the characteristic methods of elaboration which set sherries apart from other wines (3).

One of the characteristic effects of biological aging is a considerable increase in the acetaldehyde produced. This compound is generally recognized as one of the major intermediate metabolites in fermentation processes and in some enzyme activities in yeast (4). Hence, the increase in concentration stems from an imbalance between production and consumption, indicating progressive deviation of the cellular metabolism. It is also worth noting the increase in acetaldehyde content when passing from the sobretablas stage (where the biological process is not sufficiently stable) to the first stage of the solera system (where this process is already becoming regulated).

As for the evolution of the volatile compounds studied, it is worth noting the decrease in acetate concentration (directly connected with the yeast's metabolic activity mentioned above). Its consumption is not, however, very great because there is a smaller proportion of esters than of ethanol, although it is sufficient to be detectable.

The concentration of the remaining alcohols increased from the 1st criadera to the solera stage in roughly the same proportion as the initial quantity. According to the results shown in this study, the increase may be set at 20%. This fact can be explained as a consequence of the phenomenon of selective penetration of compounds through the wood of the butts and of the biological activity of the yeast.

It has been shown that vegetal fibers of the wood tend to permit the preferential evaporation of water molecules through the wood while preventing the passage of other molecules. As a consequence of this phenomenon, called "merma," the volume of liquid lost per year of aging is

Table 5. Parameters of the Amontillado-type wines studied according to aging stages.

Parameter	(Units)	Aging stage Sra *	3Cra	2Cra	1Cra	Sra
Alcohol grade	(°GL)	14.6	16.8	17.4	17.7	18.0
TA	(g tartaric/L)	3.95	4.87	5.25	5.65	5.80
VA	(g tartaric/L)	0.21	0.47	0.59	0.70	0.74
pH		3.43	3.25	3.24	3.23	3.23
Density	(g/mL)	0.9852	0.9848	0.9850	0.9852	0.9854
Acetaldehyde	(mmol/L)	6.54	5.82	5.02	4.56	4.24
Methyl acetate	(mmol/L)	0.36	0.30	0.41	0.43	0.47
Ethyl acetate	(mmol/L)	0.66	1.19	1.67	1.99	2.02
Methanol	(mmol/L)	2.78	3.65	4.00	4.09	4.34
n-Propanol	(mmol/L)	0.98	0.88	0.93	1.00	1.10
n-Butanol	(mmol/L)	0.08	0.05	0.05	0.07	0.07
2-Butanol	(mmol/L)	-	-	-	-	-
i-Butanol	(mmol/L)	1.22	1.46	1.48	1.51	1.55
i-Amyl alcohols	(mmol/L)	2.92	3.05	3.14	3.21	3.24

* Solera of Fino-wines systems.

estimated to be between 3% and 5% of initial volume (10).

Bearing in mind that, in the biological processes studied, total aging time is four years, 4% annual decrement would mean a 15% reduction from the initial volume. It is, therefore, highly likely that this is the major factor causing the increase in concentration.

There is also evidence for production of some alcohol (*i.e.*, *i*-butanol or *i*-amyl alcohols) by the filiform yeast (11), given that the metabolism of certain amino acids, such as valine, leucine, or *i*-leucine, can generate the corresponding alcohols through decarboxylation followed by reduction (17). Thus, part of the increase detected in concentration may be due to these processes.

Finally, it should be pointed out that the only significant difference between the two types of biologically aged wine studied (Fino and Manzanilla) lies in the final concentrations of acetaldehyde and *i*-amyl alcohols. This difference is a consequence of the different climatic conditions surrounding aging. In the case of Manzanilla wines, the climate is milder, as their elaboration takes place closer to the coast; consequently, the intensity of the yeasts' metabolism is slightly different. Furthermore, as the atmostphere is cooler and more humid, there is less water evaporation and hence less concentration effect.

Physical-chemical aging: A series of phenomena occur in physical-chemical aging which differentiates it from biological aging. First, in contrast to biological aging, total acidity increases. A similar variation is observed in volatile acidity, which increases to over 0.5 g/L (expressed as tartaric acid). These differences may be justified if one considers the effects of concentration through merma, given that in this case, aging time is much longer and its effects much more marked. Further, the oxidation characteristic of physical-chemical aging causes the formation of acid compounds, as will be explained later.

Again, there is no yeast development in this type of aging, since alcohol grade is adjusted up to about 18°GL. The absence of yeast capable of consuming the acetic acid, coupled with the concentration and oxidation mentioned above, are responsible for the increase in volatile acidity observed during aging. The combination of these factors also explains the considerable increase in alcohol grade.

The rest of the alcohols increase in concentration *ca* 30% from the 3rd criadera to the solera stage, which concurs with the estimated concentration calculated for the merma effect over the aging time studied (30% - 40%). The same concentration phenomenon should occur in the rest of the compounds studied; however, it can be observed that the concentration of acetaldehyde remains constant at *ca* 3.6 m*M* throughout aging.

If it is accepted that acetaldehyde should be subject to the same concentration effects as alcohols, this would indicate that *ca* 1 mmol/L is lost during the process. The reason for this loss lies in later oxidation of acetaldehyde and chemical combination to form ethyl acetate. The oxidation process must depend on the kinetics of oxygen absorption through the wine's surface and through the wood of the butts, since acetaldehyde oxidizes easily to acetic acid (14) and only a very slow oxidation is detected.

In line with this, there is a considerable increase throughout the process in ethyl acetate concentration. The formation of acetic acid through acetaldehyde allows the possibility of esterification with the predominant ethanol, thus forming ethyl acetate (13). The increase in this concentration to be expected of this compound, reckoning by the merma effect, would be between 30% and 40%, as previously stated; however, the increase is in fact over 65%. This means an increase in ethyl acetate concentration of *ca* 0.6 mmol/L more than was expected and demonstrates that additional amounts of this compound are formed during aging.

Both the excess of ethyl acetate and the lack of acetaldehyde show that the compounds oxidize in physical-chemical aging, unlike in the biological processes where acetaldehyde concentration increases with time. Furthermore, the oxidation and esterification processes mentioned are probably sources of the various esters and other compounds which are components of wine aroma (7,18).

There are differences between Olorosos and Amontillados despite the fact that both undergo physical-chemical aging. In effect, the final concentration of volatile compounds in the solera stage is greater in Amontillados than in Olorosos. This was to be expected since Amontillados age biologically in the first stage of the process; therefore, the initial concentration of these compounds is greater.

There is a sharp increase in ethanol content between the final aging stage of Finos and the first stage of Amontillados (from 15°GL to 17°GL) to suppress yeast growth, which should not occur in physical-chemical aging. For this reason, the concentrations of some volatile compounds may be disturbed, depending on the importance of the operation.

Finally, it is important to note that in the Amontillado-type wines studied, the amount of acetaldehyde lost from the 1st criadera to the final solera stage is an estimated 100 mg/L. This shows a greater degree of oxidation owing to the greater initial concentration. Furthermore, the final ethyl acetate concentration was *ca* 50 mg/L over the expected, which shows also that there was a greater degree of esterification. Thus, the main difference between the two physical-chemical aging processes is quantitative and results from the prior biological aging undergone by Amontillados.

Conclusions

In the Sherry region, there are several types of wine whose elaborations follow two clearly differentiated basic aging processes. One of these is essentially biological; the other is fundamentally physical-chemical.

In biological aging, a whole series of biochemical transformations take place peculiar to the metabolism of the yeasts which operate in the process. These result in the reduction, over time, of certain volatile compounds

which are important in the organoleptic characters of the wines. At the same time, there are effects which concentrate (or precipitate) other substances.

In physical-chemical aging, a general effect of concentration occurs over time. This is due to the phenomenon of merma. Compounds such as acetaldehyde, which in biological aging increase in concentration, decrease in concentration over time owing to chemical oxidation; conversely, ethyl acetate, which disappears during biological aging, concentrates as a result of another reaction.

The concentration of certain compounds, such as ethyl acetate and acetaldehyde, do not indicate solely age or the quality of the process as is the case with other wines; they also indicate the use of one or another of the aging techniques. This fact must be taken into account when formulating quality equations for these wines.

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