Dry Extract in Sherry and Its Evolution in the Aging Process

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The variation of the dry extract of sherry has been studied during its aging process. These variations have been evaluated, and it has been found that the dry extract of the wines depends fundamentally on the type of aging process to which they have been subjected. In the case of biological aging (Fino-type sherries), there is a decrease of dry extract of the wine in the aging process. This is due to the metabolism of the flor yeast of certain components of the wine, principally glycerol, and to the precipitation of potassium bitartrate during the long stocking period. For these reasons, the dry extract of wines which have been aged biologically can have values below 15 g/L. On the other hand, the dry extract in sherries which have been subjected to a physical-chemical aging process (Oloroso-type sherries) increases. This is due to the concentration of all the components of the wine produced by the evaporation in the aging. For this reason, the values of the dry extract of wines aged by this system can be over 22 g/L.

The sugar-free dry extract of a wine depends on multiple factors, ranging from the nature of the wine or of the soil and cultivation techniques to the production and aging procedure. That is why its value in a wine is used as a parameter to assess its quality or authenticity. In certain countries, the legislation specifies a minimum of 15 g/L for dry extract in wine (9).

The production of sherry is very special, the result being a distinctive product. Apart from the specific geology, climate, and vine variety, what stands out in the production process is its aging by the "solera system," which is dynamic and unique (3). At the same time, this aging can be biological in the case of the Finos and Manzanillas, physical-chemical in the Olorosos, or first biological and later physical-chemical for the Amontillados.

The dry extract will vary in each of these different aging processes, *i.e.*, the formation of a film-forming yeast in the case of the biological aging or the selective porosity of the wood toward different substances during its aging.

The development of yeast on the surface of the wine after fermentation produces important changes both in the organoleptic characteristics and the general constitution of the wine; these changes are due to the metabolism of the yeast that uses and tranforms several substances. For example, the use of glycerol by the yeast is well known (7).

On the other hand, when the aging is without biological activity and because of the continuous physical-chemical reactions of aging in wood, some compounds will concentrate in the wine (11). This is independent from the precipitations that take place because of long stocking periods and low temperatures during winter.

In this work, studies have been carried out to determine the variation of the sugar-free dry extract of sherry during its aging process. It is based on a high number of samples extracted from standard industrial processes. In addition, research has been carried out regarding the major causes of the variations detected, and the biological and physical-chemical processes have been compared.

This study shows that there is a close relationship between the levels of sugar-free dry extract in sherry and the type of aging to which the sherry has been subjected.

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, called "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 (11). Table 1 shows the average aging time for each system.

A good description of the characteristics and operation of industrial solera systems can be found in the works of Casas (3, 4) and Pérez (11).

Table 1. Average estimated aging time (in years) for each stage and type of wine studied.

Stage		Aging			
No.	Name	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

* For the Amontillado, the first four years corresponds to biological aging in a Fino system.

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Table 2. Analysis of the Fino sherries studied in their different stages of aging.

Parameter	(Units)	Stages of aging S/T	3Cra	2Cra	1Cra	Sra
Alcohol	(°GL)	16.0	15.4	15.1	14.8	14.6
Total acidity	(g TH_2/L)	5.27	4.98	4.78	4.37	3.95
Volatile acidity	(g TH_2/L)	0.39	0.38	0.30	0.24	0.21
pH		3.26	3.16	3.20	3.28	3.33
D 20/20	(g/mL)	0.9874	0.9862	0.9859	0.9857	0.9856
Tartaric acid	(g TH_2/L)	3.31	2.69	2.57	2.34	2.20
Potassium	(g K/L)	1.24	0.77	0.79	0.82	0.82
Sulfate	(g SO_4/L)	0.85	0.74	0.68	0.66	0.66
Phosphate	(g PO_4/L)	0.07	0.06	0.06	0.06	0.05
Total nitrogen	(g N/L)	0.34	0.30	0.29	0.28	0.27
Protein index	(g/L)	2.14	1.89	1.83	1.76	1.70
Glycerol	(g/L)	7.08	2.49	1.19	0.45	0.14
Polyphenol index	(g GH/L)	0.39	0.30	0.32	0.33	0.34
HDE	(g/L)	20.3	15.7	13.9	12.6	11.9

For every one of the 20 aging systems studied, 50-mL samples of wine were taken out of every butt from the center. 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.

Sample analysis: pH was measured with a digital pH meter, equipped with a combined electrode. Total acidity was determined by titration according to the methods of the American Society of Enologists (1). Volatile acidity and alcohol grade were determined by the O. I. V. standard volumetric method (8) and a Dujardin-Salleron-type ebulliometer (2), respectively. Density (D20/20) was measured using the pycnometric method (16).

Glycerol and total nitrogen were determined using a standard enzymatic test (5) and the Kjeldhal method (10), respectively. Protein index was calculated from the value of total nitrogen and using the normal factor for proteins in fruits (6.3 mg protein index/mg total nitrogen (2)). Tartaric acid content was measured using the Rebelein modified method (14), and the polyphenols index was calculated by the Folin-Ciocalteu method (17). Orthophosphate was determined using the colorimetric method based in the ascorbic acid reactivity (18).

Sulfates were measured by the gravimetric method with barium salt (15) and potassium by atomic absorption (4). Hydrometric dry extract (HDE) was calculated from the official normative in quality control (16).

Results and Discussion

The general plan of this study has been established so as to evaluate the variation of the hydrometric dry extract (HDE) in wines during their aging; for this purpose, the variations of a series of substances have been compared in the course of the process. Separate studies have been done for biological and physical-chemical aging in view of the different evolutions of the HDE in both.

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 include results of the wines which have had biological aging, and Tables 4 and 5 are the results for the wines of physical-chemical aging.

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.

Also, the statistical treatment shows that there are no significant differences between solera systems of the same type.

Biological aging: One can see that the HDE levels

Table 3. Analysis of the Manzanilla sherries studied in their different stages of aging.

Parameter	(Units)	Stages of aging S/T	3Cra	2Cra	1Cra	Sra
Alcohol	(°GL)	16.0	15.2	14.9	14.7	14.5
Total acidity	(g TH_2/L)	5.27	4.94	4.65	4.54	4.24
Volatile acidity	(g TH_2/L)	0.39	0.40	0.38	0.36	0.27
pH		3.26	3.16	3.19	3.29	3.32
D 20/20	(g/mL)	0.9874	0.9860	0.9859	0.9858	0.9856
Tartaric acid	(g TH_2/L)	3.31	2.35	2.30	2.21	2.19
Potassium	(g K/L)	1.24	0.75	0.79	0.81	0.81
Sulfate	(g SO_4/L)	0.85	0.80	0.75	0.74	0.74
Phosphate	(g PO_4/L)	0.07	0.08	0.08	0.10	0.10
Total nitrogen	(g N/L)	0.34	0.30	0.32	0.36	0.35
Protein index	(g/L)	2.14	1.89	2.02	2.27	2.20
Glycerol	(g/L)	7.08	2.99	2.07	1.26	0.29
Polyphenol index	(g GH/L)	0.39	0.31	0.32	0.33	0.34
HDE	(g/L)	20.3	14.7	13.4	12.6	11.6

Table 4. Analysis of the Oloroso sherries studied in their different stages of aging.

		Stages of aging				
Parameter	(Units)	S/T	3Cra	2Cra	1Cra	Sra
Alcohol	(°GL)	18.2	18.9	19.1	19.4	19.6
Total acidity	(g TH_2/L)	4.80	5.43	5.53	5.59	5.59
Volatile acidity	(g TH_2/L)	0.69	0.90	1.03	1.15	1.15
pH		3.16	3.46	3.43	3.39	3.35
D 20/20	(g/mL)	0.9841	0.9835	0.9840	0.9844	0.9848
Tartaric acid	(g TH_2/L)	1.96	1.27	1.05	0.92	0.85
Potassium	(g K/L)	0.75	1.00	1.12	1.22	1.30
Sulfate	(g SO_4/L)	0.88	0.98	1.15	1.22	1.32
Phosphate	(g PO_4/L)	0.10	0.12	0.14	0.14	0.15
Total nitrogen	(g N/L)	0.29	0.29	0.30	0.31	0.34
Protein index	(g/L)	1.83	1.83	1.89	1.95	2.14
Glycerol	(g/L)	6.40	6.92	7.68	8.04	8.83
Polyphenol index	(g GH/L)	0.31	0.38	0.41	0.43	0.46
HDE	(g/L)	18.0	18.5	20.3	22.4	24.0

for wines aged biologically are already quite low in the intermediate stages of the process; this results in the wines from the solera stage, which are the wines to be sold commercially, having a hydrometric dry extract below the standard.

Nearly 60% of the HDE in Fino sherries and over 60% of the HDE in Manzanillas is composed by only seven substances. These results can be seen in the tables. The three substances which contribute most to the value of the HDE are glycerol, tartaric acid, and nitrogenous compounds. To a lesser extent, we find potassium, sulfates, and polyphenolic compounds. The concentration of inorganic phosphorous has also been taken into consideration, although its influence is much less than that of the other six substances.

The variation in concentration of these substances during the process shows in the first place a strong reduction in the levels of tartaric acid, which produced a considerable decrease in total acidity. The principal cause of this reduction is the precipitation of potassium bitartrate, which is produced by the significant increase in the degree of alcohol after the traditional fortification process of sherry (from 12°GL after fermentation to 16.5°GL for Finos and 18°GL for Olorosos) and by the long storing time and low temperature of winter.

The precipitation of 1.1 g/L tartaric acid in the form of potassium bitartrate should produce a reduction in the concentration of potassium in solution of approximately 0.3 g/L. However, this reduction is in fact 0.4 g/L, which means that there must be small amounts of precipitation of potassium as other insoluble salts under these conditions.

There is also a reduction in the concentration of sulfates during the process which is also due to precipitation with several cations. All these precipitations tend to diminish as a result of the medium, caused by the fortification and other factors. The reduction in sulfate can reach values above 0.1 g/L.

Glycerol is the most important compound in the evolution of the dry extract. The reduction in glycerol during the biological aging will represent *ca* 80% of the decrease of the HDE. This important reduction in the concentration of glycerol is explained by the biological nature of the process.

In the course of its metabolic activity, the yeast consumes a series of components such as ethanol, glycerol, and acetate. These constitute its source of carbon matter and are transformed into fatty acid, triglycerides, enzymes, or other macromolecules which become part of its cell structure (4).

The protein index also has a considerable reduction in its value during aging. This reduction is due to the assimilation of the protein by superficial layers of the yeast in its growth. This layer of the yeast is being

Table 5. Analysis of the Amontillado sherries studied in their different stages of aging.

		Stages of aging				
Parameter	(Units)	S/T	3Cra	2Cra	1Cra	Sra
Alcohol	(°GL)	14.6	16.8	17.4	17.7	18.0
Total acidity	(g TH_2/L)	3.95	4.87	5.25	5.65	5.80
Volatile acidity	(g TH_2/L)	0.21	0.47	0.59	0.70	0.74
pH		3.43	3.25	3.24	3.23	3.23
D 20/20	(g/mL)	0.9852	0.9848	0.9850	0.9852	0.9854
Tartaric acid	(g TH_2/L)	2.20	1.46	1.33	1.18	1.09
Potassium	(g K/L)	0.82	1.07	1.20	1.36	1.44
Sulfate	(g SO_4/L)	0.66	1.38	1.63	1.95	2.13
Phosphate	(g PO_4/L)	0.05	0.05	0.06	0.07	0.08
Total nitrogen	(g N/L)	0.27	0.26	0.28	0.32	0.34
Protein index	(g/L)	1.70	1.64	1.76	2.02	2.14
Glycerol	(g/L)	0.14	2.05	2.53	3.59	4.37
Polyphenol index	(g GH/L)	0.34	0.40	0.45	0.50	0.51
HDE	(g/L)	10.8	15.9	18.3	19.6	20.9

continuously regenerated, while the dead yeast will fall to the bottom of the butt where it will accumulate in the form of proteic matter. It is worth noting that this index undergoes an important reduction from the first to the second stage of aging, and from then on, it is less pronounced.

This evolution, which is similar in other substances, is due to the fact that the first stage of aging is static (the sherry of vintage is not moved from its butt); on the other hand, the rest of the aging stages is a dynamic process (solera system). In this way, the composition in the first stage will be that of the specific vintage, and as we progress in the scales, these characteristics will be buffered, giving way to the particular effects of the aging system.

The only significant difference that one can detect between the two types of wine (Fino and Manzanilla) that have been aged biologically is in the intensity of some of the aforementioned effects. In general, the transformations observed are the same. The small differences found in the concentration of some substances are the results of different climatic conditions during aging. In the case of Manzanilla, the climate is more humid and moderate in temperature because its aging takes place in an area close to the sea; this brings about a difference in intensity of the metabolism of the yeast.

The variation in the concentration of the seven substances studied represents the total reduction of the HDE found in the aging of Finos, as can be seen in Table 2.

For the Manzanillas, they will represent also the total reduction of HDE (Table 3). These facts sufficiently explain the reduction in general of the dry extract of the sherries which have been submitted to biological aging.

Physical-chemical aging: Wines subject to physical-chemical aging will have considerably higher values of HDE than those aged biologically due to the lack of yeast that uses up the different compounds previously mentioned. The film-forming yeast will not live on the Olorosos or older stage of the Amontillados because of their higher alcohol content.

It is proven (11) that the vegetal fibers of the oak wood in the butts will allow the evaporation of water molecules through the wood but will prevent passage of organic molecules. Due to this effect, the liquid lost each year in the aging can be estimated to be 3% to 5% of the initial volume (11), and many substances will increase their concentrations accordingly. As a result, the dry extract will also rise.

The same substances studied in the biological aging will, in this case, represent more than 50% of the HDE of the Amontillados and more than 60% of the Oloroso sherries. Nevertheless, the variations of concentrations of these substances will represent nearly 60% of the rise in value of the HDE of the Amontillados and nearly 50% of the Olorosos. It is therefore evident that, in physical-chemical aging, substances other than the seven studied also play an important part in the variations of HDE. To go a step further, it is probably not simply a question of variation in the concentration of individual substances, but rather of the sum of the increases in a whole series of substances as a consequence of the loss effect mentioned above.

This is consistent with the fact that the total increase of the HDE in Olorosos is 33% with respect to the initial value. Also, this concentration value is within the estimated range of increase for loss effect on the studied aging period (30% - 40%).

For Amontillados, the HDE level increases in a higher proportion; in other words, there must be other factors, additional to the loss effect, which will assist this phenomenon.

Looking into the variation of the substances studied, one can see that all have a great increase in their concentrations. In some substances such as potassium, values will be higher than those estimated in the loss effect. This implies an ion exchange process with the wood of the butt that also helps in the loss effect (12).

In the case of the Amontillado sherries, one has to bear in mind that the first stages in aging are biological and the rest physical-chemical and that between them, there is a fortification which will bring about the inactivity of the yeast. This operation will naturally produce certain alterations in the variation of the typical concentration of some of the substances in the wine.

There are also some substances that have a similar evolution in both aging processes. This is the case with tartaric acid, which will always (with favorable levels of alcohol, potassium, and temperature) precipitate as potassium bitartrate. It has been proven that at a higher alcoholic degree, higher concentration of potassium in solution, and lower temperatures, the precipitation is greater. Moreover, due to the existence of two successive equilibria in the deprotonation of tartaric acid, it is known (13) that the precipitation of potassium bitartrate provokes a reduction in the pH value if this value is under 3.5 and an increase if the precipitation is provoked at a pH above 3.5. This will explain the variations of the pH found during the initial stage of aging.

The polyphenol index also increases in both aging processes, although to a higher degree in physical-chemical aging. In this case, it is due to a longer-lasting process which helps the evolution of polyphenols in their oxidative and polymerization path.

Conclusions

Only seven substances constitute *ca* 60% of the dry extract in Fino, Manzanilla, Amontillado, and Oloroso sherries. These substances are initially glycerol, tartaric acid, and proteins and secondly polyphenols, potassium, sulfates, and orthophosphate.

The difference between the initial and final values of dry extract in the aging are due to the variation in the concentration of these substances. In biological aging, reduction in HDE is totally accounted for; in physical-chemical aging, HDE increase is accounted for to the extent of 50% to 60%.

The principal causes of these variations in concentration are the precipitation of potassium bitartrate during

both types of aging, the use of organic matter by the film-forming yeast in the biological aging, and the concentration by the loss effect in the physical-chemical aging.

The fact that the content of HDE in sherries aged biologically does not exceed values of 15 g/L and, on the other hand, wines that are subject to physical-chemical aging can exceed values of 22 g/L, is therefore explained.

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