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Changes in Polyalcohol and Phenol Compound Contents in the Ageing of Sherry Wines

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ABSTRACT

The changes occurring in polyalcohols and non-flavonoid phenol compounds during ageing in eight sherry wine Solera systems (Fino, Amontillado and Oloroso) were studied. The highest polyalcohol content was found in the Olorosos, the Finos having the lowest. Mannitol and sorbitol contents were negligible in several samples of Fino wine. Polyalcohols did not follow any regular pattern of variation during the ageing process in the wines studied.

In most of the systems the aldehydes and total phenolic acids underwent a steady increase during ageing. However, studies of the trend followed by each individual phenol component showed considerable differences, even between systems used to produce the same type of sherry. Such differences may have been due to differences in how the various bodegas carried out the sherry wine ageing process.

INTRODUCTION

Sherry wines are marketed after a complicated maturation process that varies in length, lasting not less than three years. During this time the wine acquires its typical characteristics through the changes taking place in its composition. Ageing is carried out by means of a procedure known as the Solera system. This system consists of a series of butts holding sherry in the process of ageing, so arranged as to provide for progressive fractional blending. It is composed of a varying number of stages. Stage 1 contains

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the oldest wine and, from it, the finished wine is drawn. When drawing off wine, the butts are only partially emptied (no more than one-third of their contents at a time). Butts in stage 1 are immediately replenished from stage 2, which, in turn, is replenished from stage 3, and so on. The stage with the highest number contains the youngest wine and it is replenished with young wine or with wine kept in butts for about a year (*añada*). Details regarding the production of different types of sherry wines in Spain were described by Casas (1969).

During the ageing of Fino wines, the alcohol level must be kept between 15% and 15·5%. This allows growth of 'flor yeast', which forms a film over the wine in the butts. In the case of Oloroso wines, the alcohol level is increased to 18%. At this alcohol concentration flor yeast films do not form. Amontillado wines are made from Finos already matured for several years; the alcohol content of this wine is raised to 18% and it is then aged in a manner similar to that for Oloroso wines. From a practical standpoint, it would be extremely interesting to establish the precise length of time needed to age each type of wine prior to bottling, in view of the rising costs involved in ageing these wines. In order to be able to accurately ascertain the optimum ageing time, variations taking place in the different components of the wines during the process must be determined in detail.

Phenol compounds are a very important component of sherry wines. The source of such compounds is traceable both to the must and to the wooden butts in which the wines are aged. Any alterations affecting the phenol compounds will have a direct or indirect effect on the organoleptic properties of the wine (Paronetto, 1977). In addition, polyalcohols, with the exception of glycerol and 2, 3-butylene glycol, make up a group of substances which have not, to date, been the subject of much study in connection with wine, while their presence in sherries was recently established (Olano, 1983).

The authors recently examined the changes occurring in polyalcohols and phenol compounds during the ageing of Fino and Oloroso wines in two Solera systems (Estrella *et al.*, 1983; Olano, 1983). Because of the small number of samples studied, no final conclusions could be drawn. The purpose of the present study was to gain a more detailed knowledge of the changes taking place during the ageing process. To this end, variations in the polyalcohol and non-flavonoid phenol contents were studied in eight Solera systems from different bodegas in the Jerez de la Frontera district.

MATERIALS AND METHODS

Wines

Eight Solera systems from different bodegas (large wine cellars) in Jerez were analysed. Three were Fino Soleras (aged in the presence of a flor yeast film), three Oloroso Soleras (aged in the absence of a flor yeast film) and two Amontillado Soleras (Fino subsequently aged in the absence of the flor yeast film). Stage 1 contained the oldest wines, stage 4 the youngest.

Analysis of polyols

One millilitre of wine containing 0·3 mg of perseitol added as the internal standard was evaporated to dryness under vacuum at 60 °C and treated with 1 ml of acetic anhydride and 0·2 ml of pyridine for 1 h at 100 °C. After evaporation of the acetylation reagent, the alditol–acetate mixture was dissolved in 0·4 ml of dichloromethane and applied to the gas chromatograph as a 0·6 μl sample.

Gas–liquid chromatography (GLC) was carried out using a Sigma 3B gas chromatograph equipped with a capillary column, 25 m × 0·25 mm inside diameter, with OV–101 as the stationary phase. The oven temperature was 210 °C for 25 min which was raised to 240 °C at a rate of 39 °C a minute.

Analysis of phenol compounds

A hundred millilitres of wine were treated three times with 10 ml of ethyl ether. The ethereal fraction (30 ml) was dried with sodium acetate and evaporated to dryness under vacuum, then dissolved in 1 ml ethanol:water (50:50) and applied to the chromatograph as a 5 μl sample.

The analysis was accomplished using high performance liquid chromatography (HPLC) employing a Waters Associates (model 6000A) chromatograph equipped with two 6000A pumps, a model 660 solvent programmer, a U6K injector, a model 440 detector and an RCM-100 radial compression module with an 8 mm C_{18}, 5 μ Radial-Pak column. Solvent A was 2% (v/v) acetic acid in water. Solvent B was acetic acid/methanol/water (2%, 30%, 68%, v/v). Operating conditions: solvent program, 5, 25 min, 0·0 to 100% B; solvent flow rate, 1·7 ml/min. The detector wavelengths were 280 and 340 nm.

Identification of components was effected by comparing the retention times of peaks with those of pure standards and by measuring the response ratios at 280 and 340 nm. Quantification was achieved by comparing the height of peaks in the sample with those of standards.

RESULTS AND DISCUSSION

Figure 1 shows a chromatogram for the acetylated derivatives of one wine. The Figure shows that the polyalcohols do not interfere with the monosaccharides present in the wines; hence, polyalcohol determinations could be carried out without prior separation of reducing sugars.

Tables 1, 2 and 3 show the values for the erythritol, xylitol, arabitol, inositol, mannitol and sorbitol contents in the different systems studied. It will be noted that the polyalcohols did not generally undergo constant variation, although they did increase or decrease over the maturation process. Conversely, after an initial rise or fall recorded for most samples, subsequent variation tended to follow just the opposite trend. This would appear to indicate that the differences in the composition of the various *añadas* employed in the Solera systems were more pronounced than possible changes occurring due to ageing.

TABLE 1
Contents of Polyalcohols in Three Solera Systems of Fino Sherry Wine

System	*Stage*	*Polyalcohols (mg/litre)*					
		Erythritol	*Arabitol*	*Xylitol*	*Mannitol*	*Sorbitol*	*Inositol*
F	4	117	26·4	36·3	Traces	58·6	334
	3	127	23·6	38·7	25·1	73·1	374
	2	122	27·3	41·4	Traces	65·5	295
	1	123	25·7	36·6	Traces	12·7	268
G	4	124	17·0	24·8	Traces	33·7	111
	3	123	21·4	28·1	Traces	Traces	74·2
	2	140	24·1	31·8	Traces	Traces	174
	1	130	24·8	30·8	Traces	Traces	269
H	4	105	18·7	22·4	57·3	40·8	372
	3	128	30·4	31·4	72·2	49·6	171
	2	141	22·5	47·5	58·9	55·1	13·2
	1	141	28·8	46·3	56·7	55·9	20·9

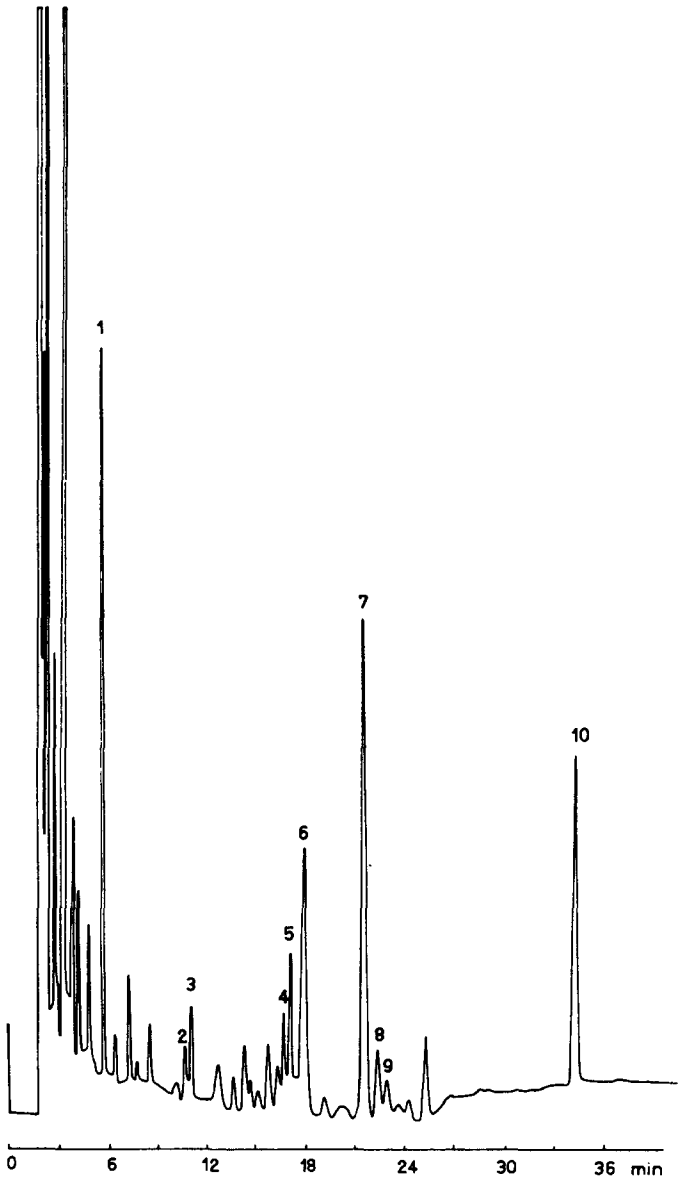

Fig. 1. Chromatogram of acetylated polyalcohols of a wine sample. 1. Erythritol. 2, Arabitol. 3, Xylitol. 4 and 5, Fructose. 6, Glucose. 7, Inositol. 8, Mannitol. 9, Sorbitol. 10, Perseitol (internal standard).

TABLE 2
Contents of Polyalcohols in Two Solera Systems of Amontillado Sherry Wine

System	*Stage*	*Polyalcohols (mg/litre)*					
		Erythritol	*Arabitol*	*Xylitol*	*Mannitol*	*Sorbitol*	*Inositol*
D	4	150	24·7	45·8	55·6	42·8	418
	3	197	24·2	64·3	64·8	46·9	480
	2	110	23·3	75·9	85·2	61·6	534
	1	236	30·9	73·4	93·7	69·5	542
E	3	180	26·6	64·6	112	79·3	48·1
	2	191	23·5	55·7	98·9	72·0	62·6
	1	130	27·6	35·5	106	55·0	424

The erythritol, xylitol and arabitol contents were similar for all three types of sherry whereas inositol, sorbitol and mannitol were more abundant in the Olorosos than in the other types of wine. In the opinion of some authors (Valentinis & Mattioni, 1968; Amerine *et al.*, 1972), mannitol is always a bacterial spoilage product from the reduction of fructose, and sorbitol may be produced either by the yeasts during fermentation or by fungus infection of the grapes or must (Triquet-Pissard, 1981). Mannitol was not detected in system G or in system F

TABLE 3
Contents of Polyalcohols in Three Solera Systems of Oloroso Sherry Wine

System	*Stage*	*Polyalcohols (mg/litre)*					
		Erythritol	*Arabitol*	*Xylitol*	*Mannitol*	*Sorbitol*	*Inositol*
A	3	187	21·7	53·2	173	71·7	132
	2	192	28·3	79·5	237	74·3	481
	1	325	61·4	149	348	134	854
B	4	151	24·7	45·8	55·5	42·8	418
	3	197	28·2	53·2	65·0	46·9	463
	2	110	24·2	64·3	85·2	61·6	534
	1	236	30·9	75·9	93·7	69·5	541
C	4	158	24·3	53·1	488	94·1	320
	3	168	22·3	53·4	731	115	301
	2	150	26·0	53·1	489	89·9	350
	1	175	42·0	85·0	716	117	465

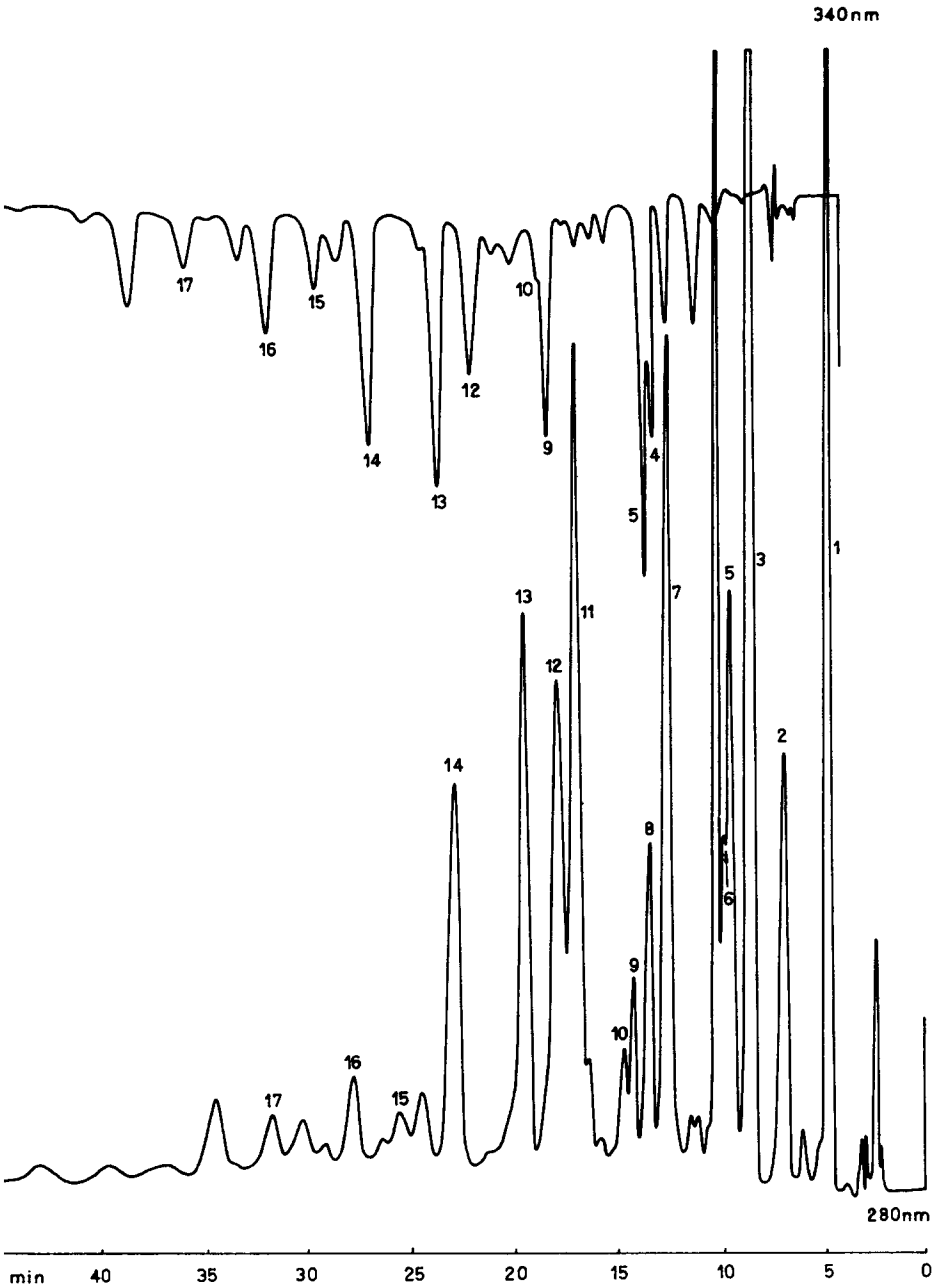

Fig. 2. HPLC chromatograms of phenolic compounds of a sherry wine. 1, Gallic acid. 2, Protocatechuic acid. 3, Hydroxymethylfurfural. 4, Gentisic acid. 5, 3,4-Dihydroxybenzoic aldehyde. 6, *p*-Hydroxybenzoic acid. 7, *p*-Hydroxybenzoic aldehyde. 8, Vanillic acid. 9, Caffeic acid. 10, Esculetin. 11, Syringic acid. 12. *p*-Vanillin. 13, *p*-Hydroxycinnamic acid. 14, Syringic aldehyde. 15, Ferulic acid. 16, Scopoletin. 17, Coniferaldehyde.

(except in stage 3), possibly due to the absence of bacterial contamination. Appreciable amounts of sorbitol were detected in system F, whereas, in system G, it was detected only in the fourth stage. This would seem to confirm that the microbial contamination that gives rise to mannitol is not the same type that yields sorbitol.

Figure 2 shows a chromatogram from HPLC analysis of the non-flavonoid phenol compounds in a sherry wine. Coniferaldehyde (peak 17) was only found in Amontillado and Oloroso wines. Quantification of this substance was subject to considerable error; hence, it has not been included in the results of this study. Tables 4, 5 and 6 summarize the changes taking place in the phenolic acids in Oloroso, Fino and Amontillado wines. Generally speaking, the benzoic acids underwent an increase during the maturation of all three types of wine. Gallic acid increased during the ageing of Finos, whereas, in Amontillado and Oloroso wines, there was no regular pattern of increase or decrease. The same applied to protocatechuic acid in system G for Fino wine, in which the values in stages 2 and 3 were much lower than those for stages 1 and 4. A low cinnamic acid content was recorded in the Fino wines, with slight variation taking place during ageing, except in system H, where the caffeic, *p*-hydroxycinnamic and ferulic acid contents in stages 2 and 3 were quite different from those in stages 1 and 4. Slight variations in the cinnamic acid content were observed in the Amontillados, except in system D, in which the *p*-hydroxycinnamic acid content rose during the ageing process. No changes were observed in the Oloroso wines, except in the case of stage 3 in system A, which had a low ferulic acid content, and stage 1 in system C, in which the contents of the three cinnamic acids increased considerably.

Tables 7, 8 and 9 present the aldehyde and coumarin contents in the three types of sherry wine. The Olorosos exhibited the highest *p*-hydroxybenzoic, *p*-vanillin and syringic aldehyde levels. The concentrations of these aldehydes increased during the ageing of both Oloroso and Amontillado wines. The Finos had lower levels of these aldehydes than did the other two types of sherry, and no substantial changes in their contents were observed during ageing, except for the value found for stage 1 in system H, in which the *p*-hydroxybenzoic aldehyde content was much higher than the stage 2 value. The amount of 3,4-dihydroxybenzoic aldehyde in the Amontillados and Olorosos was higher than that in the Finos and increased in the former two types during ageing except in system B, in which the highest values were recorded for the

TABLE 4
Changes in Phenolic Acids Contents During Ageing of Fino Sherry Wine

System	*Stage*	*Benzoic acids (mg/litre)*						*Cinnamic acids (mg/litre)*		
		Gallic	*Proto-catechuic*	*p-Hydroxy*	*Vanillic*	*Syringic*	*Gentisic*	*Caffeic*	*p-Hydroxy*	*Ferulic*
F	4	82·3	252	28·3	40·0	38·5	56·6	11·4	14·4	
	3	86·7	248	28·7	46·3	42·3	75·6	11·0	10·2	
	2	118	214	26·4	48·1	52·1	68·4	10·2	6·0	
	1	126	215	26·9	54·2	54·0	61·2	10·4	6·0	
G	4	96·1	178	60·0	47·6	6·8	20·0	8·2	10·6	10·4
	3	78·1	90·6	44·2	44·2	25·6	21·4	9·4	8·8	10·4
	2	82·5	90·2	40·2	47·6	28·8	21·0	7·8	8·2	9·8
	1	132	138	46·8	68·0	42·4	24·4	7·8	8·4	12·0
H	4	29·2	242	62·4	26·2	11·0	54·0	16·0	24·4	12·6
	3	61·4	204	55·2	35·8	27·8	45·0	58·4	48·0	15·6
	2	46·4	341	59·2	47·8	26·0	75·5	9·2	10·4	8·4
	1	96·4	314	69·0	91·0	70·8	82·8	43·6	36·2	30·0

TABLE 5
Changes in Phenolic Acids Contents During Ageing of Amontillado Sherry Wine

System	*Stage*	*Benzoic acids (mg/litre)*					*Cinnamic acids (mg/litre)*		
		Gallic	*Proto-catechuic*	*p-Hydroxy*	*Vanillic*	*Syringic*	*Caffeic*	*p-Hydroxy*	*Ferulic*
D	4	293	116	122	79·8	92·0	37·4	46·8	22·4
	3	273	150	148	127	113	35·0	58·4	24·6
	2	272	182	172	141	132	35·0	77·4	25·4
	1	273	167	185	119	111	33·4	78·8	29·3
E	3	289	221	74·4	52·6	34·6	82·4	64·6	22·8
	2	72·6	141	64·8	52·6	35·2	69·6	66·0	28·8
	1	111	206	70·2	80·8	53·6	72·4	62·6	19·2

TABLE 6
Changes in Phenolic Acids Contents During Ageing of Oloroso Sherry Wine

System	*Stage*	*Benzoic acids (mg/litre)*					*Cinnamic acids (mg/litre)*		
		Gallic	*Proto-catechuic*	*p-Hydroxy*	*Vanillic*	*Syringic*	*Caffeic*	*p-Hydroxy*	*Ferulic*
A	3	94·2	180	38·3	52·5	156	24·0	54·3	14·0
	2	194	278	118	138	154	36·0	102	56·5
	1	130	392	159	234	170	30·1	138	56·5
B	4	121	175	148	93·4	103	54·8	106	33·0
	3	203	179	156	107	102	35·0	103	27·0
	2	127	220	152	106	92·0	32·6	102	28·4
	1	138	201	182	118	98·4	31·8	106	28·4
C	4	105	48·2	54·2	44·2	32·0	57·4	44·0	13·0
	3	144	76·6	62·2	42·8	63·0	53·4	48·6	17·4
	2	99·6	78·2	65·0	45·4	45·4	51·4	51·6	12·6
	1	54·0	123	92·6	65·6	49·0	72·4	68·0	30·0

TABLE 7
Changes in Phenolic Aldehydes and Coumarins Contents During Ageing of Fino Sherry Wine

System	*Stage*	*Phenolic aldehydes (mg/litre)*				*Coumarins (mg/litre)*	
		p-Hydroxy-benzoic	*p-Vanillinic*	*Syringic*	*3,4-Dihydroxy-benzoic*	*Esculetin*	*Scopoletin*
F	4	4·1	25·8	16·0	28·8	30·6	54·1
	3	6·0	25·0	20·3	24·8	32·6	42·0
	2	4·3	25·8	12·1	22·2	39·2	42·5
	1	6·5	21·0	38·0	20·8	37·8	46·3
G	4	4·0	21·6	12·4	39·0	20·6	58·4
	3	4·2	17·4	10·8	23·0	30·6	45·0
	2	4·6	15·8	11·4	19·2	30·6	38·2
	1	6·2	16·8	15·4	18·4	39·2	56·2
H	4	2·4	45·6	13·0	24·8	9·0	60·6
	3	7·8	33·6	15·0	34·8	11·6	94·4
	2	5·4	33·9	15·8	27·0	18·8	87·6
	1	13·2	35·0	35·0	27·0	29·6	81·0

TABLE 8
Changes in Phenolic Aldehydes and Coumarins Contents During Ageing of Amontillado Sherry Wine

System	*Stage*	*Phenolic aldehydes (mg/litre)*				*Coumarins (mg/litre)*	
		p-Hydroxy-benzoic	*p-Vanillinic*	*Syringic*	*3,4-Dihydroxy-benzoic*	*Esculetin*	*Scopoletin*
D	4	18·0	42·4	66·4	43·0	28·8	115
	3	39·4	69·8	111	58·6	36·0	51·6
	2	46·6	82·0	123	54·6	34·2	36·0
	1	42·0	89·6	105	63·4	25·2	101
E	3	12·2	37·4	27·6	55·6	18·4	78·6
	2	10·0	41·6	34·4	45·6	16·2	85·4
	1	11·4	69·8	60·0	68·6	14·4	103

TABLE 9
Changes in Phenolic Aldehydes and Coumarins Contents During Ageing of Oloroso Sherry Wine

System	*Stage*	*Phenolic aldehydes (mg/litre)*				*Coumarins (mg/litre)*	
		p-Hydroxy-benzoic	*p-Vanillinic*	*Syringic*	*3,4-Dihydroxy-benzoic*	*Esculetin*	*Scopoletin*
	3	16·0	44·3	58·7	24·0	39·2	129
A	2	66·0	100	148	67·8	24·8	90·0
	1	76·1	170	250	88·4	25·2	98·7
	4	46·2	141	136	78·0	17·0	108
B	3	54·0	108	147	97·6	18·0	103
	2	54·6	96·4	141	93·6	19·4	112
	1	60·0	112	145	85·2	19·8	99·0
	4	11·0	33·0	21·0	48·0	28·4	42·0
C	3	16·6	53·6	43·2	41·4	31·4	52·2
	2	20·0	44·0	43·2	55·8	27·4	43·4
	1	40·2	39·2	69·0	68·6	15·2	58·0

intermediate stages. On the other hand, a decrease during ageing was recorded for Fino wine in systems F and G.

All three sherries had similar esculetin and scopoletin contents, the greatest differences being found between the stages of the same system (e.g. scopoletin in system D and esculetin in system H). In general, the esculetin content did not undergo appreciable changes during the ageing process. No regular pattern of variation was found for scopoletin, although it did increase or decrease during maturation in all three types of sherry studied.

The variations in the composition of the same type of sherry between individual Solera systems may possibly be due to the fact that each of the systems belonged to a different bodega and consequently the composition of the young wines used in each system may have differed. Furthermore, all of the systems analysed were highly complex, since they consisted of blends of wines of different vintages. Add to this the difficulty in obtaining detailed information concerning the ageing and blending processes carried out at each bodega, and it becomes extremely hard to assign any given observed effect to a particular variable in the ageing process.

During ageing, sherries lose water through evaporation, which brings about an increase in the concentration of non-volatile substances. The stages of Oloroso and Amontillado ageing differ from those of Fino ageing in two fundamental respects—the high degree of alcohol present in Olorosos and Amontillados and the presence of flor yeast in Finos. The higher alcohol content in Olorosos and Amontillados may contribute to a higher rate of extraction of substances from the wooden butts and may therefore be one of the main causes of the higher concentration of polyphenol compounds in these two types of wine.

In Amontillado and Oloroso wines the ageing condition is oxidative, while in Finos a reducing condition exists due to the presence of flor yeast. This probably hinders oxidation of the phenol compounds during the ageing of Fino wines. Nevertheless, despite the oxidising medium, the aldehyde content rose in the Amontillados and Olorosos, whereas, in the Fino wines, no appreciable increases were recorded.

In summary, during the ageing process water loss through evaporation is coupled with complicated fractional blending and extraction of wood components, as well as with flor yeast growth (in Finos) or oxidative reactions (in Olorosos and Amontillados). To understand the complex changes that occur during these processes, more research aimed at studying these processes under strictly controlled conditions, which can

be achieved by establishing laboratory scale sherry Solera systems, as proposed by Criddle *et al.* (1981), is required.

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