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Changes in gas-chromatographic volatiles of young Airen wines during bottle storage

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Twenty-six commercial Airen variety wines from La Mancha (Spain) corresponding to four successsive vintages (1990–1993) were analysed by gas chromatography (GC) and characterized through 30 minor and major volatiles. Stepwise discriminant analysis applied to the GC variables obtained showed that, as in other varietal wines, diethyl succinate content increased during 3 years of storage, whereas isopentyl acetate and 2-phenylethyl acetate decreased over this period. A progressive increase in acetaldehyde content was also detected. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The shelf-life of a wine is defined as the period of time it remains stable from a chemical, microbiological and biochemical point of view and maintains its good sensory properties. This stability can be extended by taking certain precautions with regard to both storage conditions and wine distribution.

Nowadays, there is a tendency among an important sector of the market to demand white wines that are organoleptically characterized for their noticeable fruity and fresh aroma, pale colour and elegant acid taste.

The fruity character of young white wines depends on the chemical composition of the corresponding grape, mainly on the content of terpenes, together with acetates and mono- and dicarboxylic acid ethyl esters which appear during the fermentation process. The fresh character is associated with a newly fermented wine, suggesting it can be ascribed to the most recent vintage.

Airen grape accounts for 28% of the area used for wine varieties in Spain, approximately 450 000 ha. This variety covers practically the whole of central Spain, Castilla–La Mancha. Therefore almost 100% of La Mancha wines correspond to the Airen variety, which gives rise to traditional wines with a slight aroma unless adequately elaborated. Nevertheless, the new developments introduced into wine processing (soft fining of must, use of selected starters from authocthonous flora, etc.) have resulted in Airen wines with a medium fruity character. Obviously these characteristics should be retained under the storage conditions in shops and supermarkets.

The chemical composition of Airen young wines has recently been published (Aldave *et al.*, 1993).

A large number of chemical changes occur in wines during storage, which can affect their final properties. The formation of new aroma compounds together with variations in the amounts of other existing components may take place, affecting the overall quality of the wine.

Rapp & Marais (1993) have stated that changes detected in white Riesling wines in bottles, on the basis of ten successive vintages, can be related to one of the following aspects:

1. Changes in the ester content (decrease in acetates and increase in mono- and dicarboxylic acid ethyl esters).
2. Formation of substances from carbohydrate degradation.
3. Decrease in the concentrations of monoterpene alcohols.
4. In some cases, formation of unwanted products.

With regard to this last aspect, it should be pointed out that the existence of certain norisoprenoids, which can give rise to 1,1,6-trimethyl-1,2-dihydronaphthalene, constitutes a noticeable defect (as kerosene) which some

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Riesling wines stored under adverse conditions tend to develop (Simpson & Miller, 1983). It has been observed recently that the risk of occurrence depends on the climatological conditions and the soil (Marais *et al.*, 1992).

Twenty-four months is the maximum period of storage life for optimal quality of young white wines stored in glass bottles. Therefore, other containers have been considered in order to promote a longer shelf-life.

In recent years other containers have been introduced. Estimated figures for the shelf-life of young wines in different containers have been published: when storing upright in cool conditions, storage should not exceed 24 months (Lemperle, 1994) and the horizontal storage of bottles is advisable (Seckler *et al.*, 1992).

Current applications of bag-in-box systems include their use in extending the shelf-life of wine (Anonymous, 1991; Spera, 1992), the 3-litre wine pack having been very successful (Blundell, 1993). In wines packaged in aluminium cans, acetates and ethyl esters decreased after 12 months and approximately the same happened to bottled wines (Spera & Garofolo, 1993). Hypa-S cans, an aluminium–plastic combination for bottling high-quality wines, are also recommended (Buchner *et al.*, 1989).

The relatively rapid maturation of wines in PVC bottles has restricted the storage life to 6 months (Dalpasso, 1991), but plastic bottles using multiple materials of optimum dimensions were completely satisfactory (Fava *et al.*, 1991). Finally, wine in multilayer cartons suffers losses of esters and considerable sensory damage (Spera, 1993).

The aim of this study was to follow chemical changes in the fermentation volatiles of commercial Airen variety wines during storage in glass bottles under non-controlled conditions.

MATERIALS AND METHODS

Wine samples

Twenty-six commercial young white wines, corresponding to four different vintages (1990–1993) of the Airen variety, elaborated in different cellars located within the large viticultural zone of La Mancha (Spain), bottled in green glass bottles, were purchased in shops and supermarkets.

Analytical procedure

Determination of major volatiles in the wines was carried out by adding 2-pentanol as an internal standard (IS) to 2 ml of wine. A Perkin Elmer Model 8700 gas chromatograph equipped with a flame ionization detector (FID) and a 5 m×0.85 mm i.d. micropack mixed stationary phase column (Carbowax 300 + bis-2-ethylhexylsebacate, 92:8, 4% w/w) was used (Herraiz *et al.*, 1990). The column operating conditions were the following. Carrier gas: nitrogen, 15 ml min^{-1}. Temperature programme: 50°C (7 min), then increased at 6°C min^{-1} to 130°C (15 min). Injector and detector temperature: 200°C. Injection volume: 2 μl.

For the analysis of the minor volatiles, a continuous liquid–liquid extraction was performed on 100 ml of a mixture of pentane:dichloromethane (60:40) added to 200 ml of wine with 0.5 ml of 4-nonanol (IS). The obtained extract was then concentrated by means of a Vigreux column (40 cm) until a final volume of 0.5–1.0 ml was achieved. A 2 μl volume of extract was used for GC analysis.

A Hewlett-Packard 5890 Model II gas chromatograph equipped with autosampler and FID was used for analysis of minor volatiles. A capillary column BP 21 (50 m×0.32 mm) under the following operating conditions was employed. Carrier gas: helium, 1 ml min^{-1}. Temperature programme: 70°C (5 min), increased at 1°C min^{-1} to 95°C (10 min), increased at 2°C min^{-1} to 190°C (40 min); splitless 30 s, split ratio 1:80. Detector and injector temperature: 250°C.

Statistical treatment of data

Linear discriminant analysis (LDA) was chosen since this technique allows differentiation among pre-established populations (K). Calculation is based on a step-by-step selection of the variables (m) which maximize the ratio of inter/intra variance groups. The process concludes when all samples are classified in the group they belong to, rendering unnecessary the remaining variables.

In the this work a stepwise discriminant analysis, using BMDP statistical package (Dixon, 1988), was carried out with the 26 wines to obtain the variables that best revealed differences among vintages. This program was run on a Vax 9200 computer.

RESULTS AND DISCUSSION

The minor compounds identified together with the major volatiles analysed by direct injection gave rise to a set of 30 identifying variables for each wine, as represented in Table 1, where mean values of the variables analysed for each subset are shown.

In the La Mancha region, young wines normally appear in the market during the first 3 months of the year and the wines in this study were analysed during spring 1994. Therefore, the storage time of the 1993 vintage wines can be considered to be practically negligible, whereas the storage time of the 1992, 1991, 1990 vintage wines can be taken as 12, 24 and 36 months, respectively.

The classification functions obtained after applying LDA are shown in Table 2, diethyl succinate, isopentyl acetate, 2-phenylethyl acetate and acetaldehyde being the most discriminant variables. Plotting the studied samples according to the canonical variable is reported in Fig. 1, in which three different groups can be detected (i.e. 1993, 1992 and 1990 + 1991 vintage

Table 1. Mean values (standard deviations in parentheses) for the analysed variables

Variables (mg litre^{-1})	Vintage 1993 (n=8)	Vintage 1992 (n=9)	Vintage 1991 (n=4)	Vintage 1990 (n=5)
Acetaldehyde	29.9 (15.2)	45.7 (24.5)	18.4 (13.1)	38.4 (13.3)
Methanol	101 (17.8)	109 (18.9)	107 (21.3)	128 (40.0)
n-Propanol	25.2 (3.48)	29.0 (7.9)	32.10 (5.05)	26.5 (4.1)
Ethyl acetate	47.0 (24.5)	46.2 (23.7)	40.80 (41.8)	40.9 (20.5)
Isobutanol	32.5 (13.7)	30.2 (6.2)	27 (20.2)	38.3 (5.2)
2-Methylbutanol	30.8 (11.7)	21.7 (6.5)	32.65 (27.5)	39.4 (16.7)
3-Methylbutanol	177 (70.9)	143 (37.9)	173.16 (94.6)	173 (60.4)
Isopentyl acetate	2.05 (0.92)	0.59 (0.52)	1.20 (2.18)	0.08 (0.07)
Ethyl hexanoate	0.58 (0.17)	0.58 (0.20)	0.60 (0.11)	0.49 (0.32)
Hexyl acetate	0.04 (0.03)	Trace	Trace	Trace
Ethyl piruvate	0.11 (0.12)	0.26 (0.19)	0.35 (0.31)	0.49 (0.21)
Ethyl lactate	3.34 (3.00)	6.09 (4.16)	4.86 (3.63)	6.33 (3.09)
1-Hexanol	1.30 (0.53)	1.60 (0.42)	1.25 (0.44)	1.46 (0.22)
trans-3-Hexen-1-ol	0.05 (0.02)	0.08 (0.04)	0.05 (0.04)	0.04 (0.02)
cis-3-Hexen-1-ol	0.87 (0.15)	0.90 (0.32)	0.84 (0.23)	0.57 (0.07)
Ethyl octanoate	0.79 (0.23)	0.88 (0.34)	0.87 (0.22)	0.73 (0.46)
1-Octanol	0.26 (0.23)	0.24 (0.43)	0.22 (0.06)	0.18 (0.15)
Isobutyric acid	0.43 (0.22)	0.42 (0.22)	0.31 (0.09)	0.62 (0.14)
Butyric acid	0.85 (0.26)	0.99 (0.30)	1.01 (0.40)	0.94 (0.37)
Diethyl succinate	0.92 (0.53)	2.59 (0.61)	4.62 (2.82)	9.36 (1.85)
Isovaleric acid	0.59 (0.16)	0.46 (0.12)	0.50 (0.12)	0.76 (0.32)
2-Phenylethyl acetate	0.76 (0.64)	0.15 (0.07)	0.16 (0.06)	0.24 (0.17)
1-Phenylethanol	0.12 (0.06)	Trace	0.08 (0.13)	Trace
Hexanoic acid	3.35 (1.00)	3.48 (1.59)	3.71 (1.05)	3.17 (1.82)
Benzyl alcohol	0.06 (0.03)	0.04 (0.01)	0.04 (0.03)	0.47 (0.97)
2-Phenylethanol	18.20 (8.70)	19.36 (3.74)	21.5 (9.64)	21.10 (9.28)
Cinnamaldehyde	0.65 (0.31)	1.75 (1.26)	2.87 (2.74)	3.26 (3.39)
Octanoic acid	5.65 (1.63)	6.60 (2.32)	6.63 (2.58)	5.33 (3.32)
Ethyl cinnamate	Trace	Trace	Trace	0.05 (0.05)
Decanoic acid	1.35 (0.56)	1.75 (0.79)	1.49 (0.82)	1.16 (0.82)

n, number of samples; Trace, not evaluated due to low concentration.

Table 2. Discriminant linear functions which allow classification of Airen variety wines into four different vintages

$$Z_i = \lambda_{io} + \sum_{j=1,4} X_j \lambda_{ij}$$

Variables (X_j) (mg litre^{-1})	Weighting values (λ_{ij})		
	Vintage 1993	Vintage 1992	Vintages 1990 + 1991
Diethyl succinate	2.13	1.89	3.89
Isopentyl acetate	5.43	2.09	5.94
2-Phenylethyl acetate	10.41	0.46	6.72
Acetaldehyde	−0.04	0.10	−0.04
λ_{io}	−11.08	−5.58	−17.07

wines, respectively), which enabled a 100% correct classification of the samples.

For this reason, according to Fig. 1, it can be stated that Airen wines showed significant changes within 0–12 months of storage and further changes within 12–24 months. It was also observed in these tests that subsequent variations after 36 months of storage were less relevant and, consequently, these samples are grouped in a unique set, corresponding to 1990 and 1991 vintage wines.

In Table 3 the average values and standard deviations of the most discriminant variables are shown in order to check the importance of the variations in content. According to Table 3, the increase in the succinnic acid diethyl ester content is statistically significant year by year. This change has been noted previously by other authors (Shinohara & Shimuzu, 1981), who suggested the existence of a relationship between the amounts of diethyl succinate and ethyl acid succinate and storage times. Acetates, related to both the fresh and fruity aroma, decreased significantly at 12 months of storage and afterwards. In other varieties (Rapp & Marais, 1993; Edwards *et al.*, 1985), an equilibrium is achieved within 4–6 years.

Values corresponding to the acetaldehyde content are not significantly different through time, in our case

Table 3. Mean values (standard deviations in parentheses) for the discriminant variables which differentiate wines corresponding to four vintages

Variable (mg litre^{-1})	Vintage 1993 (n=8)	Vintage 1992 (n=9)	Vintage 1991 (n=4)	Vintage 1990 (n=5)
Diethyl succinate	0.92^a (0.53)	2.59^b (0.61)	4.62^c (2.82)	9.36^d (1.85)
Isopentyl acetate	2.05^b (0.92)	0.59^a (0.52)	1.20^{ab} (2.18)	0.08^a (0.07)
2-Phenylethyl acetate	0.76^b (0.64)	0.15^a (0.07)	0.16^a (0.06)	0.24^a (0.17)
Acetaldehyde	29.9^a (15.2)	45.7^a (24.5)	18.4^a (13.1)	38.4^a (13.3)

n, number of samples.
Different superscripts (a, b, c, d) indicate significantly different mean values at the 95% confidence level, according to the Student–Newman–Keuls test.

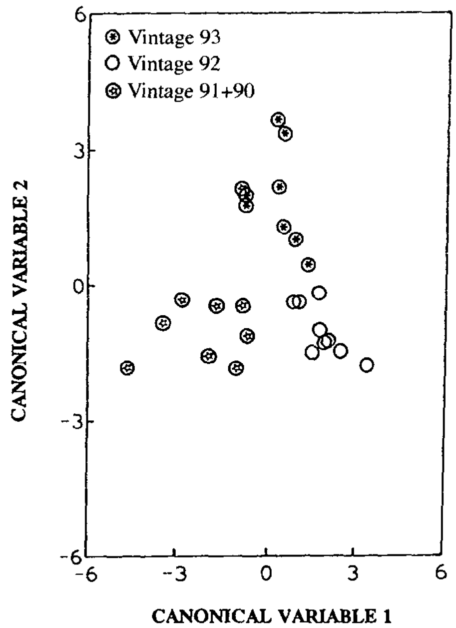

Fig. 1. Canonical plot giving the optimal two-dimensional picture of the separation of the groups.

probably because the analysis was not related to progressive storage of a unique wine. Nevertheless, it is usual among Airen wines that have not undergone an excessively long storage to possess a slight sherry character. This can also be caused by a warm environment, which is difficult to avoid in highly luminous places.

In the wines studied, other possible changes detected in other varieties (Shinohara & Watanabe, 1981; Carnacini & Del Pozo, 1986; Ramey & Ough, 1980) have not been revealed during the 3-year period considered. However, they may occur when a longer storage time is considered.

Differences found in these wines related to storage life are different from those related to other causes. In newly elaborated white wines, possible variations in higher alcohols and in n-C6, C8 and C10 acid ethyl ester contents may be due to the characteristics of the different strains of the yeasts used in fermentation (Hock, 1984).

When fermenting a unique must with different *Saccharomyces cerevisiae* strains isolated from La Mancha spontaneous flora, two strains have been found which produce 48 and 78 mg litre^{-1} of 1-propanol, respectively (22 mg litre^{-1} being the usual value in these tests), and other strains which produced 12 and 19 mg litre^{-1} of isobutanol, vs 25 mg litre^{-1}, which is the average value (Briones *et al.*, 1994). Other authors have found a strain which produced 51 mg litre^{-1} of isobutanol (Longo *et al.*, 1992). The possible formation of terpenes by yeasts does not eventually mask the composition of terpenes in grape varieties (Hock *et al.*, 1984).

On the other hand, certain differences could also be due to variations in the amounts of SO_2 used during the fermentation process (Herraiz *et al.*, 1989).

The studied wines belonged to the Airen variety and to different commercial firms and to different locations within the large area of La Mancha. Consequently, besides the parameter 'storage time', other minor factors may have contributed to differences among them.

CONCLUSIONS

Significant statistical changes in composition within 12 months of storage in bottles have been detected in young white wines of the Airen variety and in subsequent months. These changes refer to both the concentration of diethyl succinate, which increases considerably through time, and the decrease in lesser amounts of other esters such as isopentyl acetate and 2-phenylethyl acetate. Also detected has been the tendency of the acetaldehyde content in wines to increase through time.

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