ROLE OF GLYCOSIDIC AROMA PRECURSORS ON THE ODORANT PROFILES OF GRENACHE NOIR AND SYRAH WINES FROM THE RHONE VALLEY. PART 1: SENSORY STUDY

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Abstract

Aims: The aim of this study was to demonstrate the impact of the volatile compounds, arising from glycosidic precursors contained in the berries of *Vitis vinifera* L.cv Syrah and Grenache noir varieties, on wine aromas from these varieties.

Methods and results: The sensory analysis was used to compare Grenache noir and Syrah wines. The role played by the glycosidic precursors on the future odorant profile of the wines from both varieties was demonstrated in an experiment by increasing their natural content in glycosides. Then, odorant compounds were generated by aging treatments, heating at 45 °C for 3 weeks, preceded or not by enzyme addition, or natural aging for 18 months. The wines were then submitted to a selected and trained panel. Samples were compared using triangular test. Furthermore, a quantitative descriptive analysis was carried out to determine the aroma attributes describing and discriminating the wines from the two varieties.

Conclusion: The glycoconjugates increased the global aromatic complexity, and enhanced the fruity aromas in Grenache wines and the leather or olive aromas in Syrah wines. The use of glycosidase enzymes led to a stewed fruit character in Grenache wines, whereas in Syrah wines, the samples enriched with glycosides differed according to the « terroir ».

Significance and impact of study: This study showed the impact of the glycosidic fraction of the grapes on the varietal aroma of wines. Furthermore, comparisons of the results obtained by both aging techniques highlight the experimental interest of the aging model but also its limits.

Keywords: wine, aging, aroma precursors, glycoconjugates, sensory analysis, Grenache noir, Syrah

Résumé

Objectif: L'objectif de ce travail est d'étudier l'impact des composés volatils issus des précurseurs glycosidiques du raisin sur l'arôme des vins des variétés de *Vitis vinifera* L. cv Syrah et Grenache noir.

Méthodes et résultats : La comparaison des profils odorants des vins de Grenache noir et de Syrah a été réalisée par analyse sensorielle descriptive. Le rôle joué par les précurseurs glycosidiques sur le profil aromatique de ces variétés a été démontré lors de deux expérimentations utilisant des vins enrichis en glycosides. Dans la première, la libération des composés odorants a été accélérée par un procédé de vieillissement artificiel (chauffage à 45 °C pendant trois semaines), précédé ou non d'un traitement enzymatique. Dans la seconde, un élevage naturel témoin de 18 mois a été effectué sur les mêmes vins initiaux. Les deux groupes de vins ont été dégustés par deux panels de dégustateurs sélectionnés et entraînés. La différence entre les échantillons a tout d'abord été validée par un test triangulaire. Les résultats de l'analyse descriptive ont été traités par analyse de variance et par analyses multivariées afin de déterminer les descripteurs différenciant les vins des deux variétés et leur lien avec les précurseurs glycosylés.

Conclusion : L'addition des glycosides augmente l'intensité aromatique globale, développe le fruité des vins de Grenache et les notes cuir et olive des vins de Syrah. L'utilisation d'enzymes glycosidases conduit à une apparition de l'arôme fruit cuit sur les vins de Grenache, alors que les vins de Syrah ont tendance à se différencier selon le terroir.

Signification et impact de l'étude : Cette étude montre l'impact de la fraction glycosidique des raisins sur l'arôme variétal des vins. De plus, la comparaison des résultats obtenus avec les deux techniques de vieillissement met en lumière l'intérêt expérimental du vieillissement artificiel mais aussi ses limites.

Mots clés : vin, vieillissement, précurseurs d'arôme, glycosides, analyse sensorielle, Grenache noir, Syrah

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INTRODUCTION

Grenache noir and Syrah *Vitis vinifera* L.cv. are the most significant red varieties of the French Rhone valley appellations. Moreover, they are also very widespread in the South of France as well as in several other countries. Although aromatically neutral, these grapes yield wines with complex, characteristic aromas. Indeed, Grenache wines present notes of dry fig, liquorice, cherry jam and pepper (Ormières *et al.*, 1997), whereas Syrah wines can exhibit non-berry aromas: stalky, earthy, cigar/tobacco (Abbott *et al.*, 1991). The origin of these aromas present in wines aged in non-oxidizing conditions, is linked to odorless precursors present in the grape berries. Among these aroma precursors, one family was particularly studied: the glycosidic precursors (Cordonnier and Bayonove, 1974; Williams *et al.*, 1982; Voirin *et al.*, 1992; Francis *et al.*, 1999). Glycosidic compounds are composed of an aglycone moiety and a saccharide moiety linked by a β-glucosidic bond. Therefore, these compounds constitute a reserve of volatile compounds, liberated in the wines after aging (Francis *et al.*, 1992; Gunata *et al.*, 1993), that are sometimes odorant but more often, can become odorant after different transformation reactions. In neutral varieties like Syrah or Grenache noir, the glycosidic fraction of the wine aroma is proportionally more important than the free fraction (Abbot *et al.*, 1989; Razungles *et al.*, 1993; Lopez-Tamamez *et al.*, 1997). The glycosides are located in the different plant organs. In the vine, they can be ten times more abundant in the leaves than in the berries, as observed by Wirth *et al.* (2001). In the berry, the distribution can differ from one variety to another, but the skin contains the major part, between 60% and 75% of glycosides in both white (Wilson *et al.*, 1984; Gunata *et al.*, 1985) and red varieties (Gomez *et al.*, 1994). Glycosides appear at the time of veraison and accumulate during ripening and over-ripening of berries (Williams *et al.*, 1984; Wilson *et al.*, 1984; Marais, 1987; Park *et al.*, 1991; Razungles *et al.*, 1993).

Several works support the hypothesis of a biosynthesis *in situ* in the berries, which is independent of the well known processes associated with grape ripening. Indeed, Gholami *et al.* (1995) have demonstrated that the presence of glycosides in the berries is determined rather by the grape genotype than the vine genotype. Moreover, the accumulation process of glycosides and free volatiles is significant only in the late stages of ripening after sugar production slows down. For the Syrah variety, this process could occur after the interruption of exchanges between the bunch and the vine-stock which is observed through a loss of weight in the berries (Coombe and McCarthy, 1997; McCarthy and Coombe, 1999). Lastly, Bureau *et al.* (2000) have shown that light environment on the grapes influences the glycoside contents in Syrah berries.

In the wines, the major part of the odorant compounds results from the fermentation stage (Vernin *et al.*, 1987) but, except for varietal thiols generated by the yeast from cysteinylated precursors (Tominaga *et al.*, 1995), these aromas which are present just after the fermentation are not likely to create a varietal differentiation (Lopez *et al.*, 1999). On the contrary, the glycoconjugates contribute to the aroma typicity developed during Grenache noir and Syrah aging. Among them, several compounds belonging to two families of glycosides (terpenols and C13-norisoprenoids) are modified during aging to give birth to odorant compounds (Simpson, 1978; Williams *et al.*, 1980; Simpson and Miller, 1983; Rapp *et al.*, 1985; Gunata *et al.*, 1986). In the same time, some other compounds like linear esters can disappear during aging and modify the global aromatic perception of the wine. However, the major influence on the wine aroma compounds generated by glycosides was observed using gas chromatography-olfactometry (Lopez *et al.*, 2004). Indeed, Grenache noir wines, enriched with glycosides after aging model treatment, give sensory profiles close to Grenache wines aged during several years (Ormières *et al.*, 1997). This study can be taken as preliminary evidence of the role of glycosidic precursors. In the same way, Abbott *et al.* (1991) have shown the implication of glycosides in the qualitative differences between Syrah wines. However, none of theses studies has provided a comparison between the sensory profiles of wines of both varieties, on the basis of their glycoside content in the berry. Although it is difficult to separate the effects of the different varietal compounds on the wine aroma, the purpose of the present paper is to determine if there is a sensory difference between the aroma profiles of both types of wines, and to define the role played by the glycosidic precursors in generating this difference.

MATERIALS AND METHODS

1. Wines

Six vineyard plots situated in different terroirs in southern Côtes du Rhône region were selected for this experiment. Three are planted with Syrah [Cairanne SC (30 years old), Gadagne SG (12 years old), Saint Laurent des Arbres SL (30 years old)], three with Grenache noir [Bourg-Saint-Andréol GB (20 years old), Rousset les Vignes GR (20 years old), Violès GV (20 years old)]. These vines were more than ten years old. About 15 kg of grapes were harvested in 2001, at full maturity. The natural potential alcohols (% vol.) were respectively 13.4; 13.7; 13.6 for Syrah wines and 13.6; 14.7; 14.4 for Grenache wines. These six grape samples were vinified according to the standards of micro-vinifications applied in the experimental cellar of Inter Rhone.

The experimental protocol consisted in comparing samples of control wines (samples T1 and T2 below) with samples of wines, the glycosidic precursors of which were added at twice their natural content (enrichment factor = 3). The extracts of glycosides used in the enrichments were prepared with a part of the wines, after clarification.

2. Wine glycosidic fractions

Pools of glycosidic precursors from wines were obtained by extraction on Amberlite resin XAD-2 (Fluck, St-Quentin Fallavier, France) adapted from the method proposed by Günata *et al.* (1986) and Voirin *et al.* (1992).

A solution of sodium hydroxide at 32% was added to 6 liters of wine in order to adjust the pH to 7. The neutralized wine was concentrated under partial vacuum at 45 °C to lower its alcohol degree under 5 °GL, added with 120 g of polyvinylpolypyrrolidone resin and stirred for 20 minutes, then filtered on Büchner. The filtrate was then distributed into four fractions of 1.5 L. Each fraction was passed through a column containing 120 mL of XAD-2 resin, previously activated by successively passing through 500 mL of methanol, 500 mL of diethyl ether and 500 mL of Millipore water. The volatile fraction was eliminated by elution with azeotrope pentane/ dichloromethane mixture 2: 1 (v/v).

The glycosidic precursors were eluted with 1 L of methanol. The four methanolic eluates were pooled, concentrated under vacuum at 35 ° C to dryness, then washed with 4 x 100 mL of azeotrope pentane/ dichloromethane mixture 2: 1 (v/v). The extract was added with methanol and divided into four fractions, used in the different methods of the enrichment trials carried out . The fractions were dry concentrated and were stored at – 20 ° C before use.

3. Accelerated aging and natural aging of wines samples

Each natural wine was enriched with its own glycosidic fraction with a factor of 3. Thus, a glycosidic extract corresponding to 1.5 L of wine was added with 0.75 L of wine and transferred to a 0.75 L bottle (enriched wine D). 0.75 L of enriched wine with enzyme addition (DE) was prepared using 37 Milligrams (5 g/hL) of a commercial enzyme preparation (AR2000, DSM, Delf, Netherlands) containing the following glycosidase activities: β-D-apiofuranosidase (564.6 nkat/g), α-L-rhamnopyranosidase (236.7 nkat/g), α-L-arabinofuranosidase (13,500 nkat/g), α-L-arabinopyranosidase (576 nkat/g), and β-D-glucopyranosidase (4,380 nkat/g). The bottles were stoppered with screw caps under CO_2 atmosphere, homogenized, then stored at room temperature for one week. Then, each varietal wine sample was treated according to:

a) Either accelerated aging, by heating at 45 °C for three weeks (Francis *et al.*, 1994), three preparations were used:

- *T2-Mod* : Non enriched wine heated at 45 °C for three weeks,

- *D-Mod* : Enriched wine heated at 45 °C for three weeks,

- DE-*Mod* : Enriched wine with enzyme addition heated at 45 °C for three weeks.

The control wine for these samples was the T1-*Mod* non enriched wine, stored at 4 °C for three weeks.

b) Or natural aging, by storage in a cellar a t 13 °C for eighteen months:

- T2-*Nat* : Non enriched wine stored for 18 months at 13 °C,

- D-*Nat* : Enriched wine stored for 18 months at 13 °C,

- DE-*Nat* : Enriched wine with enzyme addition, stored for 18 months at 13 °C.

The control wine for these samples was the T1-*Nat* non enriched wine, stored for 18 months at 4 °C.

To differentiate these preparations, they were coded with the letters S or G (for grape variety) followed by the letter indicating the plot they came from (see above). In the Gadagne plot, the quantity of Syrah harvested was not sufficient to obtain all experimental preparations, so that the enriched and heated samples of Syrah G (SG-D-*Mod* and SG-D-*Nat*) were discarded. Thus the sampling comprises 23 trials: 11 with Syrah and 12 with Grenache for each aging mode. At the end of the accelerated aging, the samples were stored at 4 °C for 15 days, before being assessed by sensory analysis.

The natural aged samples were assessed at the end of 18 months storage. Because of the interval in time between the two series of sensory analysis due to natural aging, two different panels carried out analysis for the two types of aging.

4. Sensory analysis protocol

The sensory analyses were respectively performed in the sensory laboratories of INRA in Montpellier (artificial aging) and of Inter Rhone (natural aging) at the end of the respective aging period. Wine samples (25 mL), stored at 4 °C were presented at 17 °C, in random order, in coded (with a three digit number) tulip-shaped glasses covered by Petri dishes. The olfactory assessment of the wines was performed by direct (orthonasal) perception.

5. Sensory comparison by triangular tests

One of the objectives of the enrichment trials was to demonstrate the role of glycosides in the aromatic differentiation of Grenache noir and Syrah wines. The general aromatic perceptions generated by the glycosides of both varieties in model solutions were compared first by triangular test. Because of the time interval induced by natural aging (18 months), different panels of trained judges performed the analysis for both aging types.

6. Panel training for descriptive analysis

The two different panels of judges consisted of 17 students from the agronomic school of Montpellier (panel 1) and 20 professionals from Inter-Rhone research station (panel 2), selected on the basis of previous experiences in wine tasting. The judges were trained in 8 sessions, according to the methodology described by NFV 09-021 norm for Quantitative Descriptive Analysis (QDA) (Stone and Sidel, 1998). They were tested and trained at identifying and scoring the perception magnitude (using a 5 or a 7 points scales) of 10 red wine aroma descriptors, with natural aroma standards and aromatized wines during the two first sessions. In the third session, a list of aroma attributes was freely generated by the panels, using direct olfaction of 5 Syrah wines and 5 Grenache noir wines, of 1994 to 1998 vintages. These lists, consisting initially of a great number of terms (respectively 170 for panel 1 and 355 terms for panel 2), were reduced by eliminating, in consensus with the panel, non convenient terms. Terms quoted less than 3 times were also eliminated. In the fourth session, the panels evaluated the presence or absence of these 73 odor attributes in 8 wines; terms quoted less than 3 times for one wine, and terms considered as redundant by the panel were eliminated, which led to consensually reduce the lists to 28 (panel 1) and 26 attributes (panel 2). In the fifth session, the panels validated natural or commercial aroma standards as references for the 28 and 26 attributes, and were trained at memorizing these references. In the sixth session, the panels were trained at scoring the magnitude of the 28 and 26 odor attributes by the olfactory evaluation of 8 wines (4 Grenache noir, and 4 Syrah wines), using a category scale from 0 (no perception) to 5 or 7 (highest perception). The data were used to select the most relevant attributes from the correlation matrix and the comparison of geometrical means (GM) [GM is the square root of the product of the frequency quotation (*F*) with the relative intensity (I): GM = $(F \times I)^{1/2}$] which, by consensus, led to a reduction of the lists to 19 attributes (panel 1) and 17 attributes (panel 2) (table 1). In the seventh and eighth sessions, the panels were trained and tested at memorizing the odor standards and at scoring the magnitude, using a categories scale from 0 to 5 (panel 1) or a restricted (from no perception to highest perception) but non graduated scale (panel 2), of the 19 and 17 descriptors. These analyses were carried out in 7 wines, with duplication of 3 wines to observe the repeatability and homogeneity of the panels. In the ninth session, each panelist scored the magnitude of the 19 and 17 attributes in the two series of 23 experimental samples, using a categorical scale.

Table 1 - Aroma attributes used for the sensory analyses of wines added with glycosides and submitted to two aging treatments

Panel 1 (accelerated ageing)		Panel 2 (Natural ageing)	
Vegetal	Thyme	Vegetal	Garrigue
Minty	Pepper	Dry vegetal	Pepper
Rose	Toasted	Strawberry	Toasted
Violet	Nut	Jam	Blackcurrant
Blackcurrant	Vanilla	Candied fruits	Leather
Cherry	Cocoa	Fruits in alcohol	Black olive
Strawberry	Leather	Dry fruits	Undergrowth
Prune	Olive	Liquorice	
Jam	Undergrowth	Vanilla	
Liquorice		Cocoa	

7. Data acquisition and treatment

Two systems of data acquisition and statistical treatments were performed using tasting cards which where read by a scanner (Ulisi software, Serisud, Montpellier, France) (panel 1) or (Fizz© software, Biosystèmes, Dijon, France) (panel 2). Two-ways (samples x judges) analyses of variance (ANOVA), associated with Duncan multiple-comparison tests were performed on sensory means to test individual reproducibility, panel homogeneity and the differences between wines for each attribute. Principal Component Analysis (PCA) and Factorial Discriminant Analysis (FDA) were performed to illustrate the main differences and similarities between the samples. The different statistical analyses were performed using STATLAB (Statistiques Logiciels Pedagogie, Ivry-sur-Seine, France).

RESULTS AND DISCUSSION

The accelerated artificial aging allows to obtain an odorant profile of wines, close to that observed with an aging in natural conditions over several years (Francis *et al.*, 1994). In order to demonstrate the effect of the odorant compounds coming from the glycoside precursors on the olfactory characteristics of the wines, an increased concentration of these compounds was performed in the initial wines by adding concentrated solutions of glycosides from the same wines. This process has the advantage of enhancing the sensory impact of the components coming from these compounds which is thus clearly demonstrated. However, it was first necessary to verify if enriching Grenache and Syrah with glycosidic

fractions lead to different products by artificial or natural aging.

1. Triangular test

For both aging types, natural or heating, two analyses of olfactory differences were carried out to compare Grenache to Syrah, the first one, on enriched samples (G-Dmod vs S-Dmod; G-Dnat vs S-Dnat), the second one, on enzymatically hydrolysed enriched samples (G-DEmod vs S-DEmod; G-DEnat vs S-DEnat). Results of these four triangular tests demonstrated that the difference was significant in each case, either for the D solutions ($p = 0.01$) and for the DE solutions ($p = 0.001$), thus indicating that the aromatic expression of glycosidic precursors in the model solution differentiated significantly the two varieties for the two aging modes: natural or accelerated. However, the difference seems to be more difficult to perceive in the case of natural aging preparation without enzyme addition. This could be explained by the relatively short aging period (18 months at 13 °C), the difference being increased by the aging model and enzyme addition.

2. Effect of artificial aging on the aroma of Syrah and Grenache noir enriched wine samples

For this study, the list of 19 descriptors generated by panel 1 (table 1) was used to describe the 23 preparations of the artificial aging (the preparation SG-D being absent). The comparisons of the obtained results were validated by ANOVA and using multivariate analysis.

A first ANOVA treatment showed that, on the whole, the Grenache samples differed from Syrah samples by 6 descriptors (table 2): blackcurrant and strawberry characterized the Grenache, whereas, leather, olive, undergrowth and vegetal were more prominent in Syrah wines. Furthermore, a variance analysis followed by a statistical test comparing the 4 treatment methods T1-*Mod*, T2-*Mod*, D-*Mod* and DE-*Mod* (table 2) showed that the discriminating character of 4 attributes also reflected the effect of the artificial aging, isolating the non-heated control samples: Check samples (T1-*Mod*) from all the heated samples, whether they were enriched with glycosides or not. This demonstrates the significant effect of heating, which enhances the leather and olive notes and decreases the blackcurrant and strawberry notes.

To demonstrate the effect of glycoside enrichment combined with the aging model, a statistical treatment was then carried out by discarding the non heated control samples (T1-*Mod*) from all the heated samples, independently of whether they were enriched with glycosides or not. These variance analyses identified ten attributes as significantly different between the six groups: 2 varieties (Grenache; Syrah) x 3 treatment methods (T2-*Mod*, D-*Mod* and DE-*Mod*), the different plots being regarded as repetitions for both varieties (table 3). The Duncan test emphasized a varietal difference between the heated, non-enriched check samples (group G-T2-*Mod* compared with group S-T2-*Mod*) for 5 variables: The Grenache wines were characterized by enhanced strawberry, vanilla and thyme notes, whereas blackcurrant and undergrowth were prominent in Syrah wines. The enriched Grenache wines (groups G-D-*Mod* and G-DE-*Mod*) acquired an intense blackcurrant note whereas the same preparations for the Syrah lost this note of typicity and displayed more intense leather and olive odors (groups S-D- *Mod* and S-DE-*Mod*). Enzyme addition together with enrichment and heating gave Grenache wines from group G-DE-*Mod* an additional jammy note to the detriment of the vegetal character and tended to enhance the strawberry and prune notes for this variety, but the effect was not significant. Moreover, enzyme addition seemed to have little influence on Syrah wines enriched

Table 2 - Sensory effects of cultivar and wine treatments (controlled heating, glycoconjugate addition, glycosidase enzyming) during model aging experiments.

Variance analysis of the intensity of each aroma attribute between groups (23 wine samples in total)

Aroma attribute [a]	Cultivar Effect [b]		Wine Treatment Effect [b]			
	Grenache n=9	Syrah n=8	T1-*Mod* *n= 6*	T2-*Mod* *n=6*	D-*Mod* *n=6*	DE-*Mod* *n=5*
Vegetal	B	A				
Blackcurrant	A	B	A	B	B	B
Strawberry	A	B	A	B	B	B
Leather	B	A	B	A	A	A
Olive	B	A	B	A	A	A
Undergrowth	B	A				

[a]Aroma attributes with a significant effect (ANOVA p:0.05). [b]T1-*Mod*: storage at 4 °C; T2-*Mod* : controlled heating at 45°C; D-*Mod*: controlled heating with glycoconjugate addition; DE-*Mod*: controlled heating with addition of glycoconjugates and glycosidase enzyming. When the effect is significant, the letters indicate the order of the odorant intensities, defined by Newman-Keuls tests (A>B).

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Table 3 - Global variance analyses and Ducan tests of the product effect (cultivar/wine treatment) during model aging experiments, excluding non-heated samples.

Aroma attribute [a]	G-T2-*Mod* [b]	G-D-*Mod* [b]	G-DE-*Mod* [b]	S-T2-*Mod* [b]	S-D-*Mod* [b]	S-DE-*Mod* [b]
Vegetal	AB [c]	B	C	AB	AB	A
Blackcurrant	B	A	AB	A	B	B
Strawberry	AB	AB	A	C	BC	C
Prune	AB	AB	A	B	B	B
Jam	B	B	A	AB	B	B
Thyme	A	AB	A	BC	C	AB
Vanilla	A	A	AB	B	B	B
Leather	B	B	B	B	A	A
Olive	AB	C	BC	B	A	A
Undergrowth	B	B	AB	A	AB	A

[a]Attributes with a significant product effect, using two-ways (product x judge) and three repetitions (three terroirs). Anova test (p=0,05). [b]products : cultivar (Grenache noir or Syrah)/wine treatment (see table 2). [c]For each attribute, the letters indicate the order of the odorant intensities, defined by Duncan test (A>B>C). A common letter between two products indicates a non significant difference (p=0,05).

Table 4 - Sensory effects of the wine treatment (lycoconjugate addition, glycosidase enzyming) for each of the two cultivars Grenache noir and Syrah.

	Grenache noir		
Aroma attribute [a]	**G-T2-*Mod*** [b]	**G-D-*Mod*** [b]	**G-DE-*Mod*** [b]
Blackcurrant	B [c]	A	AB
Rose	B	A	A
Prune	B	B	A
Jam	B	B	A
Olive	A	B	B

	Syrah		
Attribute [a]	**S-T2-*Mod*** [b]	**S-D-*Mod*** [b]	**S-DE-*Mod*** [b]
Blackcurrant	A [c]	B	AB
Thyme	AB	B	A
Prune	B	B	A
Jam	B	A	A
Leather	B	A	AB

a, b, c see table 2

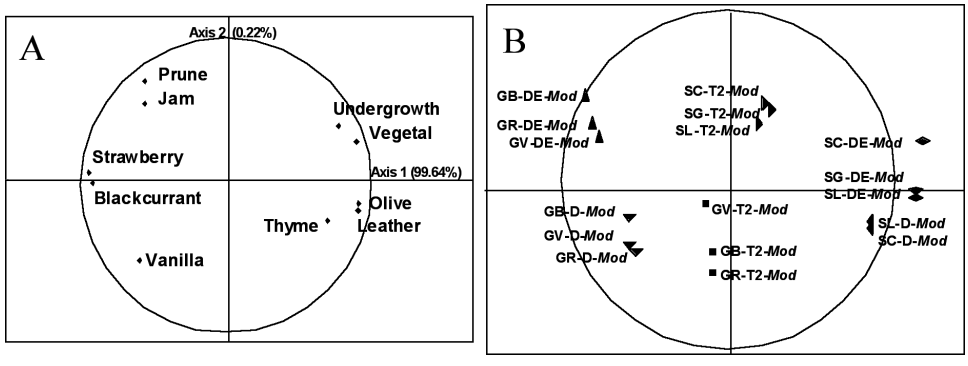

Figure 1 - Effect of glycosides on the sensory differentiation of Grenache and Syrah wines after model aging.
Factorial Discriminant Analysis (FDA) performed using the olfactive intensities of the ten attributes discriminating the 17 samples (17 wines submitted to model aging). The samples are dispatched in 6 groups Cultivar (Grenache/Syrah) x Treatment (T2-*Mod*: controlled heating at 45°C; D-*Mod*: controlled heating with glycoconjugate addition; DE-*Mod:* controlled heating with addition of glycoconjugates and glycosidasic enzyming). A: correlation circle; B: projection of the samples in the first plane (99.8 % of the total variance).

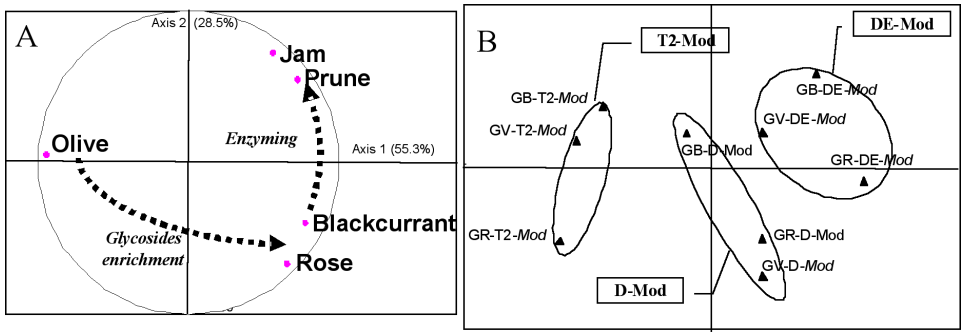

Figure 2 - Effect of glycosides on the sensory perception of Grenache wines after model aging.
Principle Components Analysis (PCA) performed using 9 samples of Grenache wine, from three different terroirs (GR, GV, GB) submitted to three treatment types (see figure 1).
The PCA uses the 5 sensory variables allowing to discriminate the treatment types (p=0.05). A: correlation circle; B: projection of the samples in the first plane (83.8 % of the total variance).

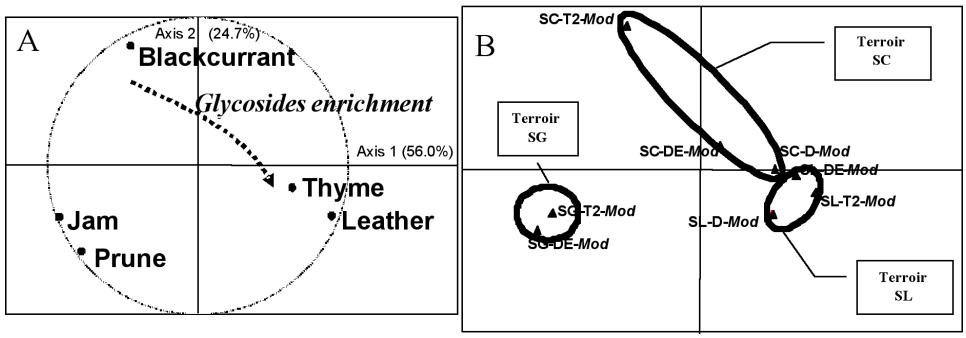

Figure 3 - Effect of glycosides on the sensory perception of Syrah after model aging.
Principle Components Analysis (PCA) performed using 8 samples of Syrah wines: wines from three different terroirs (SG, SC, SL) submitted to three treatment types (see figure 1).
The PCA uses the 5 sensory variables allowing to discriminate the treatment types (p=0.05). A: correlation circle; B: projection of the samples in the first plane (80.7 % of the total variance).

with glycosides, the group S-DE-*Mod* only differing from group S-D-*Mod* by a more intense thyme note.

Factorial Discriminant Analysis (FDA) allowed these effects to be visualized as shown in figure 1, only taking into account the 10 attributes which differentiated the six groups of samples (table 3). On axis 1, accounting for 99.6% of the total variance, the non–enriched groups G-T2-*Mod* and S-T2-*Mod*are located close to the center, whereas the samples enriched with glycosides are clearly separated according to the variety, Grenache samples are located on the left and Syrah samples on the right. Axis 2 splits the non enriched samples according to the variety (3 samples G-T2-*Mod*and 3 samples S-T2-*Mod*), as well as the Grenache samples enriched with glycosides according to the enzyme treatment (3 samples G-DE-*Mod* and 3 samples G-D-*Mod*). However, this axis accounted for 0.22% only of the total variance, which demonstrates the preponderant effect of enrichment with glycosides combined with heating.

3. Effect of artificial aging on the aroma of each varietal wine samples

Additional variance analysis combined with Duncan tests were carried out to determine the variables differentiating the heated preparations for each variety taken separately (table 4) and principal component analysis (PCA) was carried out to visualize the different effects on Grenache and Syrah respectively (figures 2 and 3).

In the PCA carried out on Grenache (figure 2), the heated samples seemed to be grouped according to the treatment (T2-*Mod*, D-*Mod* and DE-*Mod*). Variance analysis and Duncan tests shown in table 4 confirm what is observed in the figure: glycoside enrichment increases black currant and rose notes and decreases the olive note. Enzyme addition significantly develops additional stewed fruit notes: prune and jam in the DE-*Mod* samples.

In the PCA carried out on Syrah (figure 3), the samples seemed to be grouped according to the vineyard plots from which they were made: the samples from plots G are characterized by stewed fruit notes (prune and jam);

samples from plots L by thyme and leather, independently of whether they were glycoside enriched or not. Only in the case of the wine from plot C, the addition of glycosides had a most notable effect (SC-D –*Mod* and SC-DE- *Mod*), increasing thyme and leather notes to the detriment of the initial black currant note. Indeed, for the Syrah samples, the variability due to the plot is more significantly marked than that due to glycoside addition for two out of the three wines.

4. Effects of natural aging on the aroma of Grenache and Syrah wine, after glycoside enrichment

QDA analysis of glycoside enriched wines submitted to natural aging at 13° C for 18 months led to establish the olfactory profiles of 23 samples by using the 17 attributes which had been selected previously by the professionnal panel 2 (table 1). These profiles were defined by the odorant intensities perceived for each descriptor by the panelists.

A first variance analysis showed that, on the whole, Grenache samples differed from Syrah for 5 descriptors (table 5): Grenache samples were characterized by vanilla and strawberry, whereas leather, liquorice and undergrowth were more intense in the Syrah samples. For the strawberry and leather descriptors, these results confirmed the observations reported in the context of the artificial aging. Moreover, the 4 treatment modes could globally be distinguished between themselves by two other attributes, pepper and cocoa, which characterized the glycoside enriched samples (D-*Nat* and DE-*Nat*). For these last two descriptors, the samples were different from the control sample T2-*Nat* which was not glycoside enriched but had been aged in the same conditions of duration and temperature, and there was no differentiation between the control samples T1-*Nat* and T2-*Nat*.

One of the three samples of Syrah wines SG (SG-DE) differed from the others by noticeable oxidation (brown

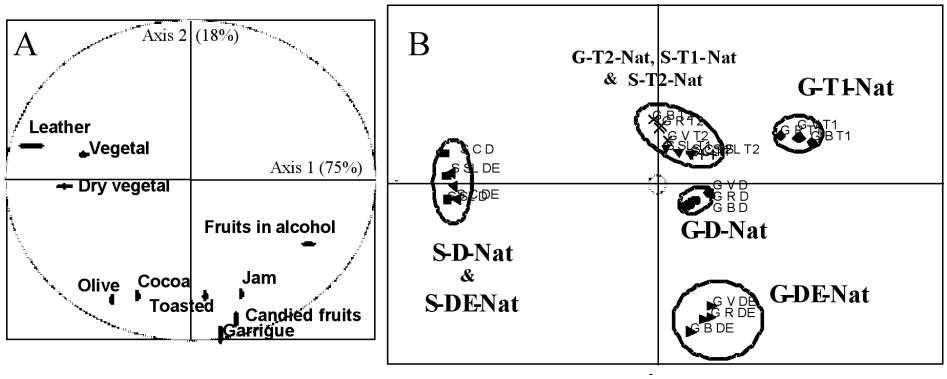

Figure 4 - Effect of glycosides on the sensory differentiation of Grenache and Syrah wines after natural aging (18 months at 13 °C).

Factorial Discriminant Analysis (FDA) performed using the olfactive intensities of the ten attributes discriminating the 24 wine samples according to the cultivar factor. The FCA uses samples dispatched in 8 groups Cultivar (Grenache/Syrah) x Treatment (T1-*Nat*: storage at 4°C; T2-*Nat*: natural aging; D-*Nat*: natural aging with glycoconjugates addition; DE-Nat: natural aging with addition of glycoconjugates and glycosidase enzyming). A: correlation circle; B: projection of the samples in the first plane (93 % of the total variance).

Table 5 - Sensory effects of cultivar and wine treatments (18 month storage, glycoconjugate addition, glycosidase enzyming) during natural aging experiments.

Variance analysis of the intensity of each aroma attribute between groups (23 wine samples in total)

Aroma Attribute [a]	Cultivar Effect [b]		Wine Treatment Effect [b]			
	Grenache	Syrah	T1-*Nat*	T2-*Nat*	D-*Nat*	DE-*Nat*
Strawberry	A	B				
Vanilla	A	B				
Liquorice	B	A				
Leather	B	A				
Undergrowth	B	A				
Pepper			AB	B	A	A
Cocoa			AB	B	A	A

[a]Aroma attributes with a significant effect (ANOVA p=0,05). [b]T1-*Nat*: storage at 13 °C; D-*Nat*: storage at 13 °C with glycoconjugate addition; DE-*Nat*: storage at 13 °C with addition of glycoconjugates and glycosidase enzyming. When the effect is significant, the letters indicate the order of the odorant intensites, defined by Newman-Keuls tests (A>B).

tinge, presence of a precipitate). Variance analysis comparing the 23 samples between themselves (table 6) confirmed this atypical character. Moreover, the corresponding Duncan tests revealed that two discriminative attributes distinguished this sample SG-DE, characterized by olive and garrigue notes abnormally intense. This sample, likely to introduce variability not representative of the studied effects, was not taken into account.

Ten out of the 17 odor descriptors used to define the profile (table 1) allowed a significant differentiation ($P < 0.05$) of at least one treatment mode in relation to the others (table 6). Factorial Discriminant Analysis (FDA) of these 10 discriminating variables for all of the 23 samples from the 8 groups: 2 varieties/4 treatment modes (T1-*Nat*; T2-*Nat*; D-*Nat*; DE-*Nat*) (plot SG being removed for the above mentioned reasons) (figure 4) emphasized the most significant variables relative to the differences between the groups. In the FDA, the first plane explains 93% of the total variance.

The non-enriched samples from both varieties (G-T1-*Nat*, S-T1-*Nat*; G-T2-*Nat*; and S-T2-*Nat*) were regrouped in the north-east zone, characterized by its aroma poverty. The first axis, 75% of the variance, essentially explains the effect of glycoside enrichment on Syrah wines. Indeed, the enriched wines S-D-*Nat* and S-DE-*Nat* presented more intense leather, fresh vegetal and dry vegetal notes, which supported the results obtained with the leather and vegetal attributes in the artificial aging experiments. The enzyme treatment did not differentiate these two groups.

The second axis (18% variance) showed the effect of glycoside enrichment on Grenache wines. In relation to the control samples G-T2-*Nat*, enrichment led to a complex aroma zone in which 6 notes were noticeable: olive, cocoa, jam, toasted, candied fruits and garrigue in G-D-*Nat* wines, which confirmed the results of artificial aging.

5. Comparisons between the different treatment modes for the same variety submitted to natural aging

To refine the effect of glycoside enrichment combined with natural aging, the discriminating variables for the samples of each variety were determined separately by variance analysis. For these ANOVA, the samples were not grouped by treatment modes due to the imbalance induced by the atypical SG-DE-*Nat* sample. For each variety, principal component analyses were carried out using the discriminating variables and the corresponding samples, excluding plot SG.

The variance analysis carried out on the Grenache samples (table 7) confirmed that 7 variables significantly differentiated the samples ($p<0.05$). These 7 variables, together with leather descriptor (significant only at $p< 5.13\%$) were selected to carry out the PCA. For the

Table 6 - Sensory effect of wine treatment (18 month storage, glycoconjugate addition, glycosidase enzyming) during natural aging experiments.

Variance analyses of the intensity of each aroma for all 23 samples

Attribute [a]	Jam	Fruits in alcohol	Candied fruits	Fresh vegetal	Dry vegetal	Garrigue	Olive	Cocoa	Toasted	Leather
P	<0.0001	<0.0001	0.0032	0.0498	0.0249	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
SG-T1-Nat	ABCDE	A	AB	ABCD	C	B	BC	A	BC	G
SG-T2-Nat	DE	AB	ABCD	BCD	BC	B	BC	DEF	C	CDEFG
SG-D-Nat	ABCDE	A	ABC	ABC	BC	A	A	AB	BC	FG
SL-T1-Nat	ABCD	CDE	ABCD	ABCD	BC	B	BC	BCDEF	C	CDEFG
SL-T2-Nat	BCDE	DE	ABCD	CD	C	B	BC	DEF	AB	DEFG
SL-D-Nat	BCDE	CDE	ABCD	ABCD	A	B	BC	ABC	BC	AB
SL-DE-Nat	ABCDE	DE	BCD	A	AB	B	BC	ABCDEF	C	CDEF
SC-T1-Nat	BCDE	DE	BCD	AB	C	B	BC	CDEF	C	BCDE
SC-T2-Nat	CDE	DE	BCD	ABCD	C	B	BC	F	BC	ABCD
SC-D-Nat	BCDE	E	BCD	ABC	BC	B	BC	BCDEF	BC	A
SC-DE-Nat	BCDE	E	D	ABCD	C	B	BC	BCDEF	BC	ABC
GR-T1-Nat	DE	CDE	CD	ABCD	BC	B	BC	EF	C	G
GR-T2-Nat	DE	BCDE	D	D	C	B	BC	CDEF	C	CDEFG
GR-D-Nat	ABC	ABC	ABCD	ABCD	ABC	B	BC	ABC	C	EFG
GR-DE-Nat	ABCDE	ABC	ABCD	BCD	BC	A	B	ABCDE	C	FG
GV-T1-Nat	CDE	ABC	CD	ABC	BC	B	BC	ABCDEF	BC	FG
GV-T2-Nat	E	DE	D	ABCD	BC	B	BC	EF	C	G
GV-D-Nat	AB	BCD	ABCD	ABCD	BC	B	BC	BCDEF	C	FG
GV-DE-Nat	BCDE	BCDE	ABC	CD	BC	A	BC	BCDEF	A	FG
GB-T1-Nat	A	BCDE	ABCD	ABCD	BC	B	BC	BCDEF	C	EFG
GB-T2-Nat	ABCDE	DE	BCD	BCD	ABC	B	C	F	C	CDEFG
GB-D-Nat	ABCDE	BCDE	ABCD	ABCD	BC	B	BC	ABCDE	BC	EFG
GB-DE-Nat	A	CDE	A	ABCD	C	A	B	ABCD	A	FG

[a]Attributes with a singificant product effect, using two-ways (product x judge) Anova test ($P \leq 0,05$ given). The products are the couple vineyard plat/wine treatment (see text and table 2). For each attribute, the letters indicate the order of the odorant intensities, defined by Duncan text (A > B > C > D > E > F > G). A common letter between two products indicates a non significant difference (p=0,05).

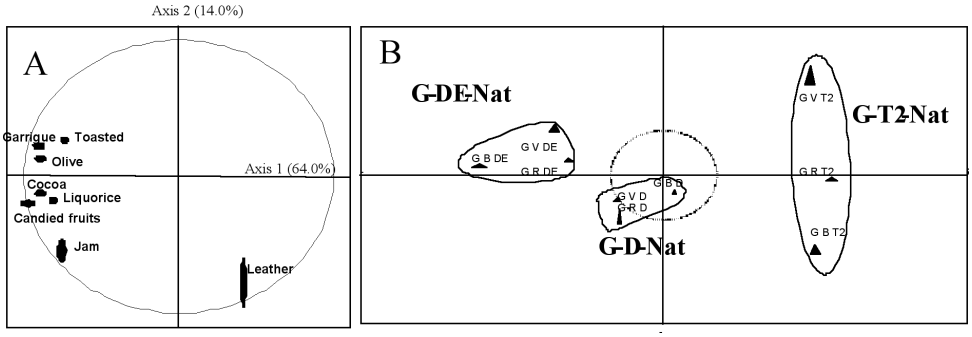

Figure 5 - Effect of glycosides on the sensory perception of Grenache wines after natural aging (18 months at 13 °C). Principle Components Analysis (PCA) performed using 9 samples of Grenache wines: wines from three different terroirs (GR, GV, GB) submitted to three treatment types (see figure 4). The PCA uses the 8 sensory variables allowing to discriminate the treatment types (p=0.05). A: correlation circle; B: projection of the samples in the first plane (78 % of the total variance).

Table 7 - Sensory effect of treatment (18-month storage, glycoconjugate addition, glycosidase enzyming) during natural aging of Grenache noir wines.

Variance analysis of the intensity of each aroma for the 12 Grenache noir samples.

Attribute [a]	Jam	Candied fruits	Garrigue	Olive	Liquorice	Cocoa	Toasted	Leather
P	*<0.0001*	*0,0029*	*<0.0001*	*0.0063*	*0.0085*	*0.0019*	*<0.0001*	*0.0513*
GR-T1-*Nat*	C	CD	B	C	B	CD	BC	BC
GR-T2-*Nat*	C	D	B	C	B	BCD	BC	A
GR-D-*Nat*	AB	ABCD	B	ABC	A	A	BC	B
GR-DE-*Nat*	ABC	ABC	A	ABC	AB	AB	BC	B
GV-T1-*Nat*	C	BCD	B	ABC	B	ABC	BC	B
GV-T2-*Nat*	C	D	B	C	B	CD	BC	BC
GV-D-*Nat*	AB	ABCD	B	ABC	A	ABC	BC	B
GV-DE-*Nat*	BC	AB	A	ABC	A	ABC	A	B
GB-T1-*Nat*	A	ABCD	B	ABC	AB	ABCD	BC	B
GB-T2-*Nat*	ABC	BCD	B	C	AB	D	C	A
GB-D-*Nat*	ABC	ABCD	B	BC	AB	AB	BC	AB
GB-DE-*Nat*	A	A	A	AB	AB	AB	A	B

[a]see table 6

sake of clarity, T1-*Nat* control samples, very similar to T2-*Nat*, were not included.

In this PCA (figure 5), the aged Grenache samples were grouped according to the three treatment modes T2-*Nat,* D-*Nat*, DE-*Nat*. Glycoside enrichment (samples D-*Nat* and DE-*Nat*) led to a complex aroma zone marked by jam, candied fruit, olive, liquorice and cocoa notes in the three T2 wines.

This effect may or may not lead to significant differences between samples, according to the plot they stemed from (table 7). At the same time, the aroma differences initially existing between the wines, particularly the leather note differentiating the GR-T2 and GB-T2 wines from the third one, decreased with glycoside enrichment. On the whole, enzyme addition emphasized this evolution in the DE-*Nat* samples by enhancing the 6 notes mentioned above, but according to the Duncan tests the effect on these attributes seemed variable according to the plots. On the other hand, the effect of enzyme addition seemed characterized by the significant appearance of additional notes like garrigue and toasted (table 7).

Variance analysis similar to those carried out on the 11 Syrah samples (table 8) showed 6 discrimating variables, 3 of which, however, were pertinent only for the samples from the atypical SG plot (fruits in alcohol, olive and garrigue). A PCA was carried out using the 3 discriminating variables for the C and L Syrah samples, but as with the Grenache samples, removing T1-*Nat* samples. This PCA (figure 6) distinguished two discriminating variables: cocoa and dry vegetal, positively correlated to the first axis (67% of the variance), which characterized the effect of glycoside enrichment. Moreover, the leather note was correlated to axis 2 (26%

Table 8 - Sensory effect of treatment (18-month storage, glycoconjugate addition, glycosidase enzyming) during natural aging of Syrah wines.

Variance analysis of the intensity of each aroma for the 11 Syrah samples.

Attribute [a]	Jam	Candied fruits	Garrigue	Olive	Liquorice	Cocoa	Toasted	Leather
P	*<0.0001*	*0,0029*	*<0.0001*	*0.0063*	*0.0085*	*0.0019*	*<0.0001*	*0.0513*
GR-T1-*Nat*	C	CD	B	C	B	CD	BC	BC
GR-T2-*Nat*	C	D	B	C	B	BCD	BC	A
GR-D-*Nat*	AB	ABCD	B	ABC	A	A	BC	B
GR-DE-*Nat*	ABC	ABC	A	ABC	AB	AB	BC	B
GV-T1-*Nat*	C	BCD	B	ABC	B	ABC	BC	B
GV-T2-*Nat*	C	D	B	C	B	CD	BC	BC
GV-D-*Nat*	AB	ABCD	B	ABC	A	ABC	BC	B
GV-DE-*Nat*	BC	AB	A	ABC	A	ABC	A	B
GB-T1-*Nat*	A	ABCD	B	ABC	AB	ABCD	BC	B
GB-T2-*Nat*	ABC	BCD	B	C	AB	D	C	A
GB-D-*Nat*	ABC	ABCD	B	BC	AB	AB	BC	AB
GB-DE-*Nat*	A	A	A	AB	AB	AB	A	B

[a]see table 6

of the variance) and distinguished the samples according to the plot they stemed from and it was particularly marked in the PC plot. Finally, for both plots, the DE samples were located in an intermediary position between T2 and D samples, suggesting that enzyme addition had attenuated the evolution.

Although the aroma notes were not comparable, like for the artificial aging, the wines from the two varieties displayed different odorant profiles due to the enrichment in glycosides. But these differences could also be explained by several other factors:

- Although they were trained according to similar procedures, the tasting panels were different. Their lists of descriptors were distinct and the meaning of the terms was specific to the panelists.

- The aging method appeared to be significant. As discussed previously, the influence of heating at 45 °C during three weeks on the aroma profiles is higher than that of natural aging in cellar during 18 months only. Thus, the generation of aroma compounds from glycosides (Zoecklein *et al.*, 1997; 1999) was more efficient under the conditions chosen for the accelerated model aging than for the natural aging (Kotseridis *et al.*, 1999).

- The sensory perception encluded interactions between odorants generated from glycosides and the other wine volatiles (Atanasova *et al.*, 2004). Thus, dimethyl sulphide (DMS), was reported to have a significant direct effect (truffle and olive notes) and an indirect effect (fruit note enhancing) on the aroma of wines from varieties like Syrah (Anocibar Beloqui, 1998; Ségurel *et al.*, 2004, 2005; Escudero *et al.*, 2007). Other compounds like fermentation-derived esters are known to decrease during aging, excepted compounds like ethyl esters of branched chain acids which increase. Some of these last compounds are characterized by red fruits odours and could also be responsible of the sensory variations observed by the judges of the two panels.

- Moreover, the « matrix » effect included also non-volatile components as polysaccharides, proteins, tannins, anthocyanins and transition metals, which could modify the gas-wine partition and the rate of the release of the odorants from the wine (Dufour and Bayonove, 1999a; 1999b; Dufour and Sauvaitre, 2000; Nedjma, 1997).

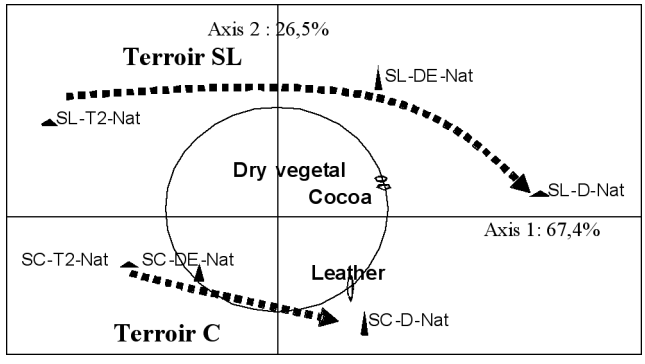

Figure 6 - Effect of glycosides on the sensory perception of Syrah wines after natural aging (18 months at 13°C).

Principle Components Analysis (PCA) performed using 6 samples of Syrah wines: wines from two different terroirs (SC, SL), each submitted to three treatment types (see figure 4). The PCA uses the 3 sensory variables allowing to discriminate the treatment types (p=0.05). A: correlation circle; B: projection of the samples in the first plane (93.9 % of the total variance).

CONCLUSION

Through glycoside enrichment combined with two aging processes, an aroma differentiation of the wines from the two varieties was observed, demonstrating that wine glycoside potential contributed to the aroma typicity acquired during aging. Enzyme addition associated to glycoside enrichment and aging seems to have a different effect according to the varieties. In accordance with previous papers (Ormières *et al.*, 1997), some aroma notes (small and candied fruits, jam, prune) were significantly revealed in Grenache wines. Enzyme addition effect was also demonstrated in Syrah wines and confirmed the previous observations (Abbott *et al.*, 1991). Aroma generation from Syrah glycosides could differ whether the hydrolysis was carried out enzymatically or chemically (Winterhalter and Skouroumounis, 1997). These results suggest that different glycoside precursors, perhaps in different concentrations, are implicated in the aroma production in the wines from both varieties. Moreover, the sensory contribution of glycosides to the aromas of Syrah wines differed from that of Grenache wines by a more pronounced effect of the plot from which they were made.

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