Aroma characteristics of Gewürztraminer grape distillate and Grappa in relation to the varietal aroma distribution in berry parts and in comparison with other monovarietal distillates.

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INTRODUCTION

More precise personality for distillates from different parts of the grape (typical of Italy, the distillates of fermented crushed grapes or "grape distillate", and direct steam distillates of fermented marc or "grappa") can be obtained for products from single particular varieties, even if not markedly aromatic. Their different aroma seldom recalls that of the relevant wines, except for the muscat distillates. This is the case of typical products from Chardonnay, Müller Thurgau and Rhine Riesling, all with a floral scent of different intensity, or from Sauvignon blanc, only rarely with a subtle vegetable aroma, or from Gewürztraminer, the most appreciated distillate, with rose and tea-like notes but, at variance with the relevant wines, not spicy at all.

A quality improvement of the different kinds of distillates can be helped by studying their particular aroma composition in relation to that of the original variety, possibly by finding sensorially important substances, and by investigating the distillation behaviour of some of them in traditional equipments. Because of real difficulties in differentiating sensorially some of these distillates and in checking their varietal purity, it is very important to find analytical parameters to be used in a statistical evaluation in order to protect the genuininess of these expensive beverages.

To this purpose, particular attention was paid in this research to the different kinds of Gewürztraminer distillates in relation to those of the other varieties, cited above.

I - MATERIALS AND METHODS

- Grappa samples of Trentino-Alto Adige region (Italy), either as commercial products or as raw high-proof distillates from the last three years, produced by four different companies, our Institute included, using traditional pot still equipment (water-bath pot stills with 6-10 plates in the rectification column (VERSINI and ODELLO, 1990). The samples (5 Chardonnay, 7 Müller Thurgau, 2 Rhine Riesling, 6 Sauvignon blanc and 9 Gewürztraminer) are representative, for each variety, of the whole yearly production for every distillery.

- Grape distillates of the same region from the varieties Yellow Muscat, Müller

Thurgau and Gewürztraminer, produced from 1990 and 1991 vintages with the same equipments.

- A series of Traminer distillates from different raw products, all coming however from a homogeneous lot of grapes, as well as the sequential samples taken during the distillation process, obtained with the pot still of the Institute.

All the samples underwent in 1991 a gas-chromatographic analysis performed by direct injection on packed and capillary columns (VERSINI et al., 1990) or, for compounds present in traces (<100 µg/l) on the same capillary columns after enrichment by liquid-liquid extraction (pentane-dichloromethane, 2:1 v/v; 10 hrs) of the distillate diluted with water to ca. 10 % vol. Statistical data treatment of the selected variables was carried out by using SAS 5.18 software on a DEC WAX 8250 computer with VMS 5 o.s..

II - RESULTS AND DISCUSSION

A - Analytical differentiation of Gewürztraminer distillates.

1 - Statistical discrimination among monovarietal grappas.

In order to perform this evaluation, among the approximately 50 compounds usually quantified by gas-chromatography with direct injection of the distillate, we considered 11 components, almost all of varietal origin, and three relevant ratios : methanol, 1-hexanol, methanol/1-hexanol (R1), trans and cis 3-hexen-1-ol, cis 3-hexen-1-ol/trans 3-hexen-1-ol (R2), β-phenylethanol (β-Ph), linalool (L), ho-trienol (Ho-tr), α-terpineol (α-T), citronellol (C), nerol (N), geraniol (G) and C+N+G/L (R3). Geraniol, nerol and citronellol are usually called "skin monoterpenols".

The values of the variables methanol and 1-hexanol can be influenced by the marc percentage of the whole distilled material and by its original fermentative status before the ensilage. On the other hand, the content of β-phenylethanol depends on the tails cut during the distillation. Absolute and relative contents of cis and trans 3-hexen-1-ol could be linked to varietal characteristics (MORET et al., 1984). The monoterpenols are the best known varietal parameters with a sensorial floral relevance. A previous study (MARGHERI and VERSINI, 1983) has shown a possible use of these compounds for an initial characterization of the varietal origin of monovarietal grappas.

The variability of the cited compounds for each variety is reported in Table 1. By PCA of autoscaled data, the projections on the plane of eigenvectors 1 and 2, or 1 and 3, explaining altogether 71.5 % of the total variance, show good separations of the Gewürztraminer group from the others (fig. 1).

By LDA as the classification technique and by using all variables, the first two functions (71.0 % and 23.8 % of the total variance, respectively), can discriminate all groups from one another, except for that of Chardonnay from that of Sauvignon grappas (fig. 2), which are separated on the plane of functions 2 and 3 (2.8 % of the explained variance) (fig. 3). The loadings of the single functions (Tab. 1a) explain the contribution of different variables to the separation among the groups. The variables Ho-Tr and R3 have, with opposite sign, the highest loading on the CAN 1 function, and therefore contribute for the most part ot the separation of the Rhine Riesling and Müller-Thurgau groups, as a whole, from the others. On the other hand, C, G, N, L, cis 3-hexen-1-ol and R2 are the most important contributors on the CAN 2 function for the separation between Gewürztraminer and Chardonnay plus Sauvignon blanc groups. The separation inside this last group can be achieved on the CAN 3 function, mostly for the prevalent contribution of the terpenols α-T and Ho-Tr, and of R1, R2 and cis 3-hexen-1-ol.

By using in the LDA procedure the first four variables from the stepwise feature selection, i.e. C, L, Ho-Tr and R2, all with Prob>F at 0.01, we can still achieve a good separation among the groups, even if there is more spread with respect to the previously cited discrimination. Rhine Riesling and Müller Thurgau groups cannot

Table 1 : mean (X) and standard déviation (S) of variables considered in the statistical data evaluation of monovarietal grappas.

GRAPPA: COMPOUND	M.THURGAU (7) X	S	RH.RIESL. (2) X	S	CHARDONNAY (5) X	S	SAUVIGNON (6) X	S	TRAMINER (9) X	S
methanol (ml % ml a.a.)	0.89	*0.23*	0.64	*0.15*	0.80	*0.16*	0.52	*0.22*	0.70	*0.22*
1-hexanol (mg % ml a.a.)	13.3	*5.6*	8.7	*0.7*	10.1	*1.9*	10.9	*2.0*	9.1	*4.1*
tr-3-hexen-1-ol (")	0.33	*0.14*	0.20	*0.02*	0.24	*0.05*	0.20	*0.06*	0.255	*0.09*
cis-3-hexen-1-ol (")	0.55	*0.21*	0.36	*0.02*	0.44	*0.15*	0.77	*0.49*	0.27	*0.105*
ß-phenylethanol (")	2.0	*0.7*	1.5	*0.1*	2.5	*1.5*	1.8	*1.1*	1.3	*0.5*
linalool (")	0.55	*0.17*	0.80	*0.06*	0.19	*0.09*	0.12	*0.04*	0.54	*0.21*
ho-trienol (")	0.21	*0.08*	0.18	*0.03*	0.023	*0.015*	0.093	*0.062*	0.058	*0.030*
α-terpineol (")	0.26	*0.15*	0.21	*0.14*	0.072	*0.024*	0.43	*0.47*	0.36	*0.20*
citronellol (")	0.037	*0.024*	0.054	*0.008*	0.029	*0.021*	0.022	*0.015*	0.34	*0.09*
nerol (")	0.072	*0.073*	0.074	*0.025*	0.063	*0.041*	0.071	*0.043*	0.36	*0.11*
geraniol (")	0.10	*0.12*	0.14	*0.04*	0.058	*0.053*	0.047	*0.012*	0.71	*0.27*
R 1	0.073	*0.024*	0.074	*0.012*	0.083	*0.031*	0.048	*0.017*	0.085	*0.035*
R 2	1.73	*0.28*	1.78	*0.13*	1.83	*0.38*	3.95	*2.23*	1.06	*0.23*
R 3	0.34	*0.21*	0.34	*0.09*	0.81	*0.43*	1.40	*1.10*	2.86	*0.92*

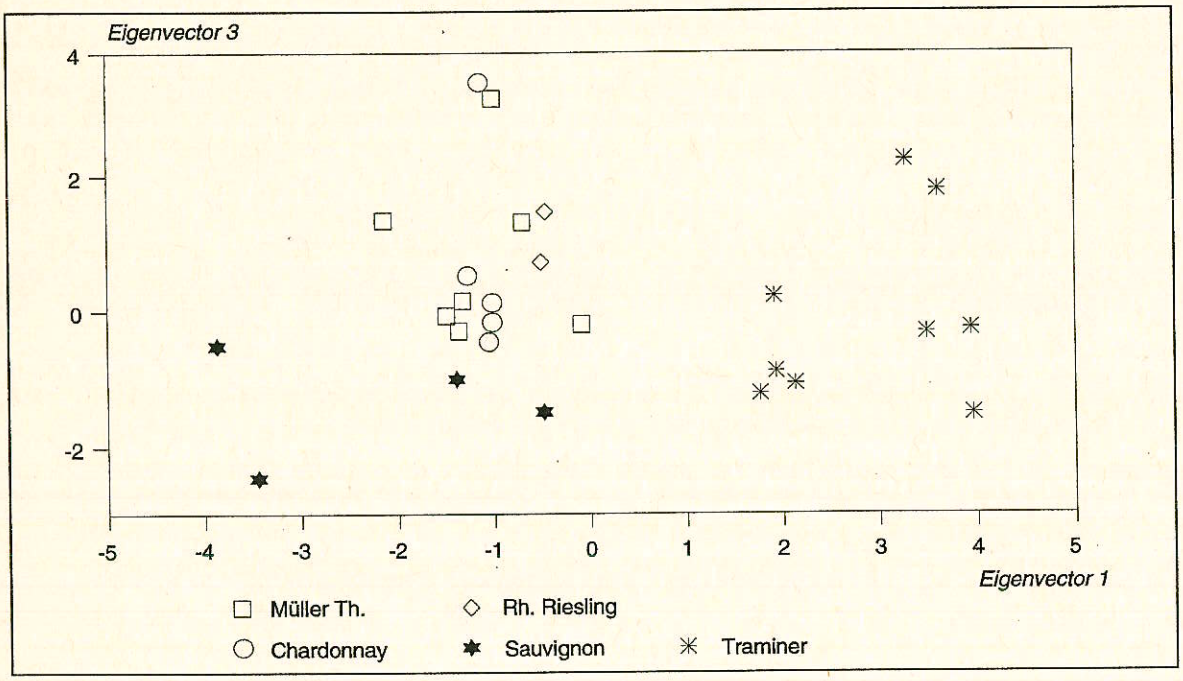

Figure 1 : PCA. Scores of data set grappas

however, be discriminated. This is shown in the plane determined by the CAN 1 and CAN 3 functions, explaining ca. 80 % of the total variance.

These results confirm the importance of the monoterpenols for a varietal classification regarding the distillate. In particular, the monoterpenols that are acknowledged to be characteristic of a given wine (RAPP et al., 1981; VERSINI et al., 1990), are also the most significant compounds in discriminating among the relevant grappas.

It is also worth mentioning the gas-chromatographic detection of a compound, present only in the Gewürztraminer distillates among many varietal products examined, some kinds of Muscat grappas included. The relevant peak area is similar to that of geraniol. Its retention time on a Supelcowax capillary column is very close to that of α-terpineol and the peak is not completely resolved. Further studies are in progress in order to identify this interesting substance.

Table 1a : results from canonical variate analysis

	1	2	3
Latent roots	38.166	12.789	1.505
Proportion var.	0.710	0.238	0.028
Cumulative var.	0.710	0.948	0.976
Variables	Standardised canonical coefficients of canonical variates		
R 1	0.041	0.308	-0.399
R 2	0.028	-0.595	0.452
R 3	0.703	0.460	0.129
V 1 (methanol)	-0.304	0.120	-0.218
V 2 (1-hexanol)	-0.280	-0.142	0.266
V 3 (tr-3-hexen-1-ol)	-0.246	0.173	0.109
V 4 (cis-3-hexen-1-ol)	-0.135	-0.497	0.441
V 5 (ß-Ph)	-0.121	-0.356	-0.191
V 6 (L)	-0.393	0.760	-0.124
V 7 (Ho-Tr)	-0.754	0.125	0.432
V 8 (α-T)	0.161	0.120	0.492
V 9 (C)	0.557	0.796	-0.018
V 10 (N)	0.544	0.724	0.024
V 11 (G)	0.494	0.768	-0.009

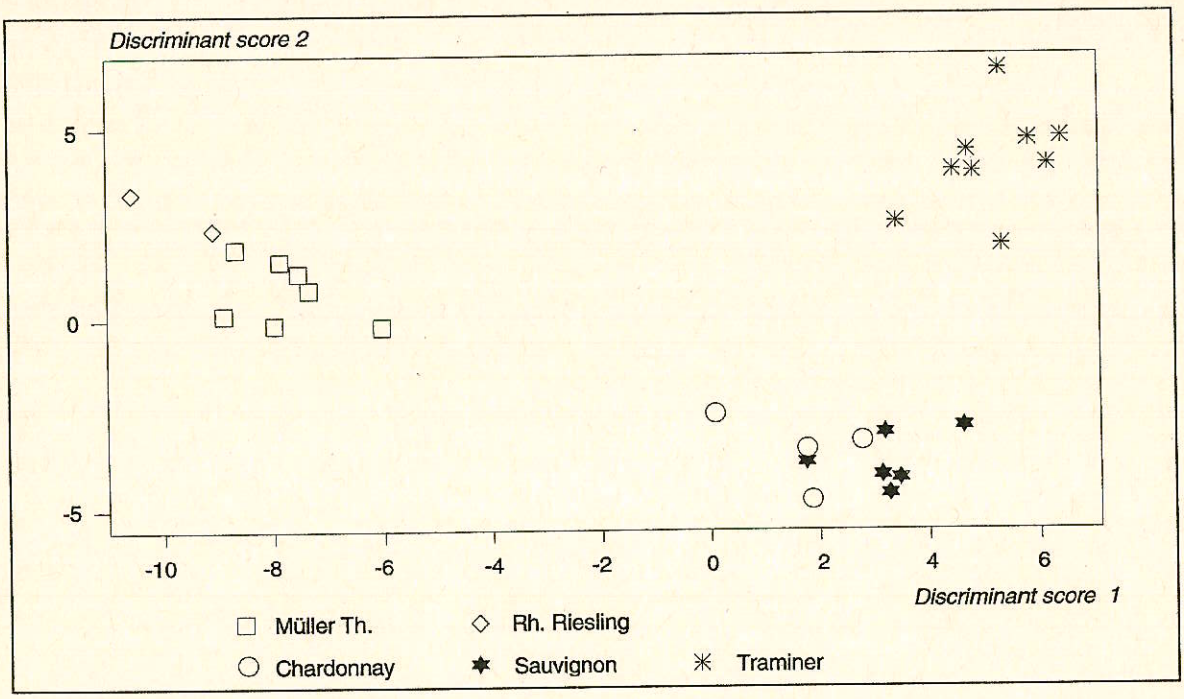

Figure 2 : LDA. Data set grappas : plot of discrim. score 1 vs discrim. score 2

2 - Considerations on the aroma characteristics of some grape distillates.

Samples of such products are in limited number and mainly obtained from average or highly floral varieties, in order to reach a sufficient aroma level from the different starting materials with respect to that for the grappa production. Thus, Chardonnay or Sauvignon grape distillates are "unsual". In this work we can only

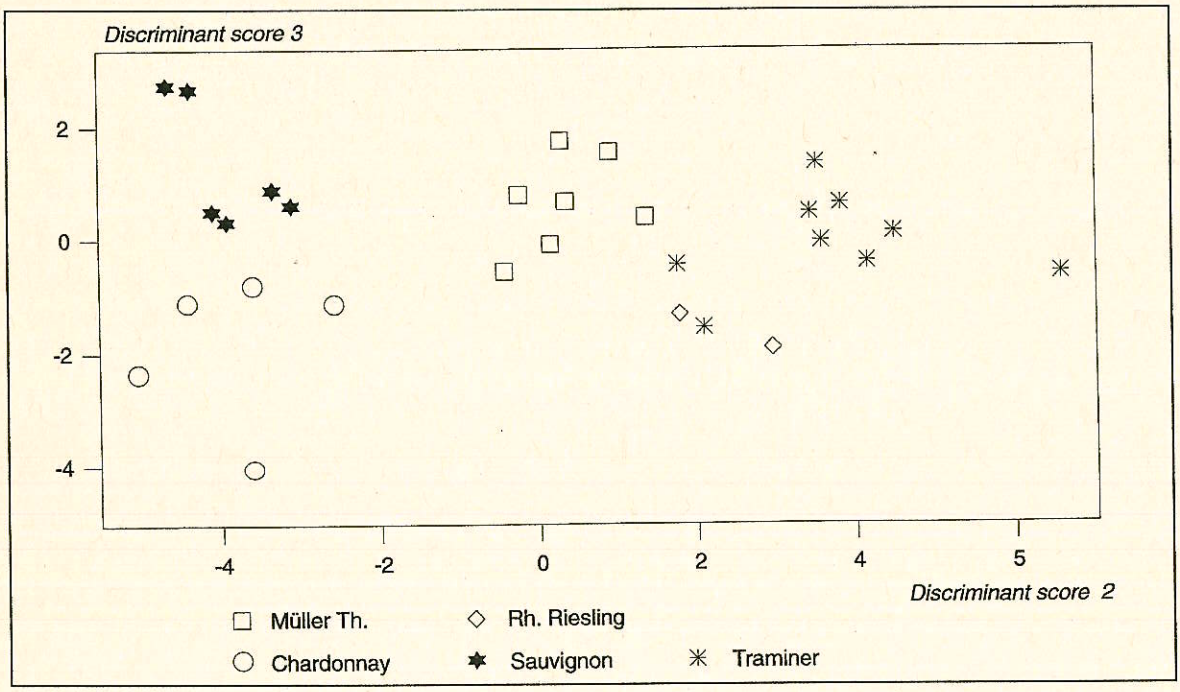

Figure 3 : LDA. Data set grappas : plot of discrim. score 2 vs discrim. score 3

deduce some compositive tendencies from the analytical results and for the varieties in Table 2, where some grape distillates of Yellow Muscat are also included for comparison.

Table 2 : mean (X) and standard deviation (S) of some variables of monovarietal grape distillates

DISTILLATE : COMPOUND	YELLOW MUSCAT (3) X	*S*	M. THURGAU (3) X	*S*	TRAMINER (3) X	*S*
methanol (ml % ml a. a.)	0.17	*0.07*	0.19	*0.08*	0.19	*0.05*
1-hexanol (mg % ml a. a.)	1.8	*0.4*	2.8	*0.6*	1.4	*0.5*
tr-3-hexen-1-ol (")	0.050	*0.016*	0.086	*0.021*	0.032	*0.021*
cis-3-hexen-1-ol (")	0.16	*0.04*	0.038	*0.019*	0.039	*0.017*
ß-phenylethanol (")	0.84	*0.48*	1.03	*0.35*	0.74	*0.66*
linalool (")	2.0	*0.25*	0.12	*0.025*	0.13	*0.01*
ho-trienol (")	1.5	*0.1*	0.16	*0.02*	0.043	*0.048*
α-terpineol (")	1.4	*0.7*	0.063	*0.030*	0.19	*0.08*
citronellol (")	1.7	*0.2*	0.009	*0.003*	0.18	*0.03*
nerol (")	0.12	*0.01*	0.013	*0.003*	0.037	*0.022*
geraniol (")	0.21	*0.02*	0.021	*0.003*	0.070	*0.036*
R 1	0.096	*0.010*	0.066	*0.017*	0.144	*0.069*
R 2	3.45	*1.32*	0.43	*0.12*	1.452	*0.910*
R 3	0.253	*0.045*	0.33	*0.12*	2.94	*1.60*

As for the relevant grappas, the higher content of L and Ho-Tr with respect to the skin monoterpenols can be confirmed for the Müller Thurgau distillates. The skin monoterpenols are once more prevalent for Traminer products. Muscat distillates, diluted about 1:10 with non aromatic products as well as less diluted Müller Thurgau grappas, could have the Müller Thurgau grape distillate aroma profile, but likely with a different L/Ho-Tr ratio, lower than 1 for the original grape distillates.

Although not reported here, additional well-known monoterpenes do not seem to improve the classification.

In Table 3, a compositive comparison among Traminer distillates produced with the same pot still, but starting from different grape derivatives coming from a homogeneous lot of grapes, is presented. The higher-alcohol profile is very similar, with a general concentration increase for the grappa. Of interest are the differences found for methanol, 1-hexanol, the varietal compounds and some ratios. the level of total monoterpenols is ca. 6 % in the wine distillate and ca. 42 % in the distillate from wine fermented with skins when referred to that in grape distillates. No variation is found for the 1-hexanol. As for the same compounds in the relevant grappa, we observed an increase to ca. 900 % of monoterpenols, as well as of the sum of the skin terpenes and of L and α-T. A tenfold increase of 1-hexanol and about fourfold for methanol are observed. The value of R3 remains about the same in products obtained from materials fermented with or without skin when distilled either in the presence or absence of skin. The composition changes discussed above could be very useful as an index for characterization and classification of starting materials for distillation.

Table 3 : comparison among distillates produced with the same pot still, starting from different grape derivatives from a homogeneus lot of Traminer grapes

COMPOUND	A	B	C	D
methanol (ml % ml a.a.)	0.02	0.17	0.20	0.74
higher alcohols (mg % ml a.a.)	226	232	216	310
1-hexanol (")	1.4	0.90	0.90	12.0
tr-3-hexen-1-ol (")	0.046	0.036	0.028	0.31
cis-3-hexen-1-ol (")	0.013	0.006	0.007	0.45
ß-phenylethanol (")	0.51	0.93	0.80	1.06
benzyl alcohol (")	0.012	0.031	0.015	0.20
linalool (")	0.030	0.027	0.054	0.52
ho-trienol (")	0.010	0.010	0.024	0.050
α-terpineol (")	0.030	0.036	0.12	1.27
citronellol (")	0.012	0.062	0.15	0.65
nerol (")	0.002	0.019	0.037	0.43
geraniol (")	0.008	0.024	0.060	1.10

A = distillate of wine obtained from free run must
B = distillate of wine separated from marcs after fermentation
C = distillate of fermented crushed grape, i.e. "grape distillate"
D = distillate of fermented marcs, i.e. "grappa"

B - Distillation behaviour of monoterpenols in comparison to that of other compounds.

This interesting aspect of the distillation process is summarized. Thus, we can confirm that :

- all primary saturated alcohols (e.g. higher alcohols, 1-hexanol and 1-nonanol) distill in the same way, preferentially in the heads and in correspondence of a strength decrease in the "heart", which is typical of the so callled "hybrid impurities";

- the esters confirm their preferential distillation in the heads, while the relevant fatty acids are mainly found in the tails;

- a different tendency (Fig. 4) is shown by the monoterpenols, i.e. the tertiary alcohols, like linalool, ho-trienol and α-terpineol, that distill preferably in the heads rather than in the tails, at variance with citronellol, nerol and geraniol. This finding is confirmed by distillation in the absence of skins and should be linked only to the different physico-chemical properties of the two groups considered.

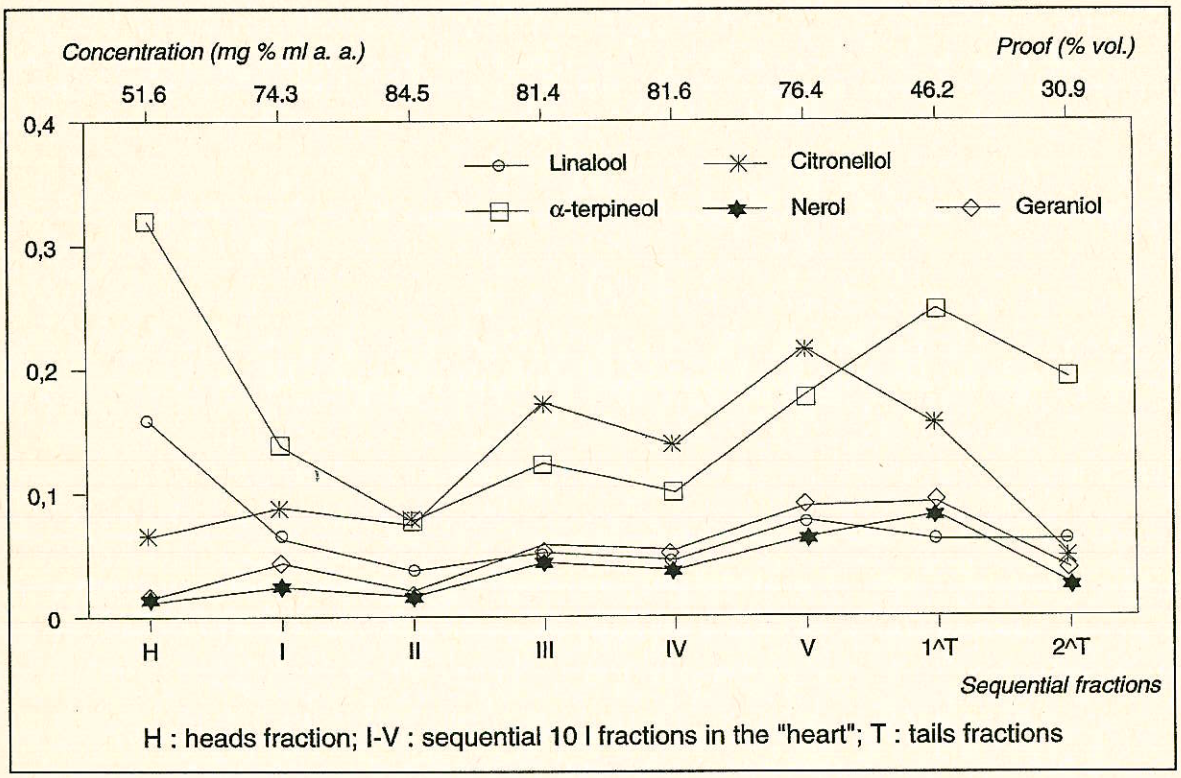

Figure 4 : distillatory behaviour of some terpenols during production of Traminer grape distillate.

III - CONCLUSION

The possibility of characterization of some monovarietal distillates with respect to the Gewürztraminer products by using a limited number of variables, mostly monoterpenols and non fermentative compounds, is discussed. For grappas, the best results were achieved by PCA and LDA data treatments, while for the small number of grape distillates only some differential tendencies were shown. A particular unidentified compound present only in Traminer distillates was shown to be present. A comparison among Traminer distillates obtained from different kinds of fermented material coming from the same lot of grapes, showed that the ratio between skin monoterpenols and other monoterpenols like linalool and ho-trienol, is linked to the presence of the marc during the fermentation of the material to be distilled, but not to its presence during the distillation. A different distillation behaviour of the tertiary with respect to the primary monoterpenols, in both cases different from that of the higher alcohols, was also shown.

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