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FREE AND BOUND GRAPE AROMA PROFILES VARIABILITY WITHIN THE FAMILY OF MUSCAT-CALLED VARIETIES

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Introduction

The different contents, mainly in Muscat varieties, of some monoterpenols, particularly of linalool with the most interesting floral scent, were established in many researches (Bayonove and Cordonnier, 1971; Usseglio-Tomasset, 1969; Terrier, 1972; Borin, 1981; Di Stefano et al., 1984a,b and 1986).

A Muscat-type aroma profile, different from that of the Rhine Riesling-type, was evidenced by Rapp et al. (1981), principally as to the relative marked content of nerol, geraniol and trans geranic acid and for the presence of 2,6-dimethyl-1,7-octadien-3,6-diol (diendiol-II). Furthermore, Di Stefano and Corino (1984a) proposed a separation within the Muscat-Malvasia group, on the basis of the marked dominance of linalool on geraniol ("Muscats") or vice versa ("Malvasias").

Additional monoterpenols and diols were identified in the meanwhile and subsequently by different research-groups, constituting altogether nowadays a group of more than 60 compounds. Most of them are found in grape also as heterosides whose structures have been for the most part elucidated. These latter compounds can be used to improve the capability of the characterization of many aromatic varieties like some Muscats and others floral and non floral cultivars, e.g. Sauvignon blanc and some clones of Chardonnay (Scienza et al., 1990; Versini et al., 1988, 1990 and 1992).

In this research - which is a part of a work regarding also other analytical and plant morphological parameters - we extended our study to the profile variability within a numerous set of Muscat-called red and white varieties. The aim was that of finding out correlations among the compounds, of discriminating and possibly grouping the varieties mainly on the basis of monoterpene descriptors, as well as of comparing some peculiarities found for this family with those for other aromatic varieties.

Materials and methods

Roughly 200 g of destemmed berries were randomly sampled from 2 kg of grapes, picked in 1989, 1990 and 1991 vintages at ripeness from at least 3 vines of 41 varieties (see the list) from the vine-collection of the Institute. List of varieties (specification for each one: label for PCA and LDA data treatments, name, possible synomym, country of the vine gift, skin colour: w=white; r=red).

(1) Muscat a petits grains, M.doré de Frontignan, G, w; (2) Trollinger Muskat, M.Hamburg (Troll.x M.Alex.), F, r; (3) Muscat fleur d'oranger, F, w; (4) Muscat à petits grains, F, w; (5) Muscat diamant, F, w; (6) Blume Muskat, Rhine Riesling x St.Laurent, G, w; (7) Muscat bifère, F, w; (8) Gelb Muscat, Précoce de Malingre, F, w; (9) Muscat d'Alexandrie, F, w;

(A) Bowood Muscat, USA, w; (B) Muscatel do Douro, P, w; (C) Muscat d'Alexandrie, Muscatel de Setubal, F, w; (D) Muscat Cluf, F, w; (F) Moscato di Terracina, I, w; (G) Muscat Blutterle, USA, w; (H) Muscat Caillaba, G, r; (I) Muscat d'Alsace blanc, F, w; Muskat Usbekistanski, YU, w; (M) Muskat Vostockni, Muskat Hamburg x Muskat Belji, YU, w; (N) Morio Muskat, Silvaner x Pinot bl., G, w; (O) Muskat Banatski, YU, w; (P) Moscato di Scanzo, I, r; (Q) Muskat Belji, YU, w; (R) Muskat Dunavski, YU, w; (S) Muscat Rouge de Madère, F, r; (T) Muskat Riesling, Rhine Riesling x St.Laurent, F, w; (U) Gelb Muscat 63/2, F, w; (V) Moscato Giallo Cl.R5, I, w; (Z) Gelb Muskateller, Muscat Blanc, G, w; (X) Muskat Trollinger, I, w; (Y) Morio Muskat, G, w; (*) Roter Muskateller (4n), Muscat Rouge, G, r; (+) Roter Muskateller, Muscat Rouge, G, r; (#) Moscato Rosa, I, r; (K) Roter Muskateller Cl.25, G, r; (=) Moscato Rosso, Muscat rouge de Madere, I, r; (%) Rosen Muskat Oberlin, Bukettraube x Courtillier M., F, w; (&) Muscatel Roxo, Muscat rouge de Madere, YU, r; (/) Moscatel rosado, ARG, r; (?) Muscat Rosä, Muscat de Marseille, F, r; (<) Muskat Ottonel, G, w.

Frozen sample handling, compounds extraction from berries and instrumental analyses were previously reported (Günata, 1984; Versini et al., 1988). The solvents chosen for a better recovery of free and bound forms by the elution from XAD-2 resin, were pentane- methylenechloride, 2/1, v:v, and ethyl acetate/methanol, 9/1, v:v, respectively. The quantified compounds were: trans and cis furan and pyran linalool oxides; linalool; ho-trienol; α-terpineol; citronellol; nerol; geraniol; 2-exo-OH-1,8-cineol; trans geranic acid; 2,6-dimethylocta-3,7-diene-2,6-diol or ho-diendiol(I); 2,6-dimethylocta-1,7-diene-3,6-diol or ho-diendiol(II); 2,6-dimethyloctane-1,7-diol; 2,6-dimethyloct-7-en-1,6-diol; (E) and (Z) 2,6-dimethylocta-2,7-diene-1,6-diol or trans and cis 8-OH-linalool; 2,6-dimethyloct-2-en-1,7-diol or 7-OH-geraniol; benzyl alcohol, 2-phenylethanol and 3-oxo-α-ionol (only as bound form).

Statistical evaluation of the data was carried out by using SAS, Genstat and SPSS-X packages.

Results and discussion

1. General considerations on the aroma profiles

Among the considered varieties, 3 of them, i.e. Muscat à petits grains, Roter Muskateller and Morio Muskat, were included with 2 or more clones to check their interclonale variability. In other cases, varieties were present with the same or similar names - mostly in different languages -, but with possible markedly different characteristics.

As suggested by literature and deduced from the analytical results, a first rough grouping among the varieties, generally with similar peculiarities in vintages, can be done just on the basis of some simple criteria. We controlled at first the total level of free monoterpenes and the content of certain free and bound monoterpenes as, for example, linalool, geraniol, diendiol I and II, and cis and trans 8-OH-linalool, these latter isomers being more interesting under the bound form. Usually, the contents were higher in 1991 vintage, with also a more marked level of cis furan and pyran linalool oxides. Above all one variety, i.e. Muscat Usbekistanski, and secondly other three, i.e. Muscat de Madeira, Précoce de Malingre (called also Gelb Muscat) and one of the examined Gelber Muskateller, were very poor in monoterpenes under both forms. However, only for the first variety this result was found in all the considered vintages and with respect to all the compounds. Thus, the Muscat Usbekistanski was left out in further discussions.

The Muscats, that resulted richer in total free terpenols, but not necessarily also in the total bound forms, were the Muscat "fleur d'oranger", the Moscato Giallo cl. R5, the Muscat Vostockni, a Muskat-Riesling coming from France and the Muskat Ottonel. They presented also the highest levels of free linalool, except for the Muscat Vostockni with a high content in free geraniol.

Some varieties, as Bowood Muscat, Blutterle Muskat, Blume Muskat (Rhine Riesling x St.Laurent) and Muscat Cluf, showed the Rhine Riesling-type aroma profile, with dominant presence of free linalool, trans pyran linalool oxide and diendiol I, and a low content in the "geraniol group" compounds (citronellol, nerol, geraniol, trans geranic acid and 7-OH-geraniol) and in diendiol II. The profile similarity was confirmed in part by the bound forms where a notable level of cis 8-OH-linalool in comparison with the trans form (Versini et al., 1992), was found, but not by cis furan

linalool oxide, α-terpineol and 2-exo-1,8-cineol, present only in traces. In this group of varieties, Blume Muskat and Muscat Cluf were richer in free and bound linalool. Nevertheless, the other declared Rhine Riesling x St.Laurent crossbreed (Muscat Riesling) cannot be included in this typology. The Caillaba Muscat, even if similar for other aspects, was different from Rhine Riesling-type because of a marked content of "geraniol group" compounds and a reduced dominance of bound cis 8-OH-linalool on the trans form. Muscat Bifere presented several analogies with Muscat Caillaba, but it singled out for the very high level of free α-terpineol with more than 400 µg/l - the Moscato di Terracina being the second more rich among all the considered Muscats with 86 µg/l - and for the ratio between geraniol and nerol under both forms, approximately at 29.

The profile common to the several Red Muscats was similar to that of the Muscat rosé (or Muscat de Marseille), as well as to that of some white muscats like the Muscat blanc d'Alsace and the Gelb Muskateller (or Muscat à petits grains). The other two Muscats à petits grains - one specified as "doré de Frontignan" - can also be included in this group. Their analytical pattern can correspond, as to the free forms similarly quantified in other researches, to that of the Italian Moscato Bianco del Piemonte (Di Stefano and Corino, 1984a), and to those of many other white Muscat varieties typical of some Italian regions (Di Stefano and Antonacci, 1986): this finding fits the plant morphological similarities.

Moreover, these results can support the possible origin of the German Roter Muskateller as a mutation of Gelber Muskateller - corresponding in its turn to the cited Italian White muscat - (Hillebrand et al., 1984), while the Yugoslav Muscat Belji ("white muscat") was significantly poorer in monoterpenes with respect to the mean of the mentioned group.

The control of the mean ratio between free linalool and geraniol can be interesting as a further varietal characterization index only at the higher or lower values, because of the marked variability induced by the vintage. Except for the already discussed Rhine Riesling-typologies and the varieties that resulted very poor in monoterpenes, ratios lower than 0.2 were found for the varieties Muskat Vostockni, Muskat Dunavski, Muskat Banatski, Moscato di Scanzo and Muscat Caillaba, and higher than 5 for Muscat fleur d'oranger, Moscato Giallo cl R5, Muskat Ottonel and Muscat Rosado. Moscato Rosa, Morio Muskat and Muscat Bifere are particularly rich in geraniol in respect to linalool as for the bound forms.

All these simple considerations based on peculiarities of the analytical profiles, can be useful to characterize roughly only some of the many considered varieties. Nevertheless, taking advantage of the high number of

available analytical parameters, we tested the possibility of a more extended discrimination among the different varieties, as well as of a selection of most significant variables leading to a synthetic interpretation of the data, by applying multivariate statistical techniques.

2. *Statistical analysis*

2a. Linear correlation analysis

All the monoterpene variables resulted linearly related to one another at a high level of significance (P>99.9%; r>0.31). The monoterpenes did not appear to be significantly related with benzyl or 2-phenylethyl alcohols - on the other hand, these are related with each other - or with the bound 3-oxo-α-ionol. These three compounds seem to be submitted to different biosynthetic variability, confirmed by the more or less normal distribution of the data with respect to the Poisson-like tailed distribution of monoterpenes.

Among the monoterpenes, more close relationships (r>0.75) regarded some groups of compounds, often in accord with previous results (Versini et al., 1992). Specifically, we cite the groups including both forms of trans furan and pyran linalool oxides, linalool, ho-diendiol(II) and (I), and trans 8-OH-linalool, those concerning geraniol, nerol, trans geranic acid and 7-OH-geraniol, or citronellol and 7-OH-citronellol, or α-terpineol and 2-exo-OH-1,8-cineol.

2b. Multivariate data treatments

Firstly, the data of 40 varieties were submitted to hierarchical cluster analysis ("average linkage between groups") performed on the free forms, on the bound forms, and on both of them altogether, respectively. Interesting classificatory results were achieved by scaling the variables to reduce their original very wide and different variability range by means of a logarithmic transformation and by considering all the variables.

The repetitions for each variety according to the vintage were allocated very close to one another in the groups, except when included in one quite big homogeneous subgroup and except for two varieties, Moscato Rosa and Moscato di Terracina.

Some simple elements useful to interpret the several groupings derived from the second principal branch, can be found in the mentioned descriptive considerations about the aroma profiles.

The secondary role of the vintage in the variety classification with this rough descriptive technique, was confirmed by LDA data treatments for all the variables, supposing a normal distribution of the logarithmic values in all

the classes. By using the 12 most discriminant variables (F-to-enter = 4.0) selected by the stepwise procedure, i.e. nerol (b); ho-diendiol (II) (f); geraniol (f); cis fur.linalool oxide (b); ho-diendiol (I) (f); α-terpineol (b); nerol (f); linalool (b); trans fur.linalool oxide (b); trans geranic acid (b); cis 8-OH-linalool (f); trans fur.linalool oxide (f), we obtained the same intervariety discrimination capability as that achieved by working with all the variables. By means of the first canonical variate, the four varieties characterized by a Rhine Riesling-type profile and the three ones that were very poor in monoterpenes, are well separated from the other cultivars, which are on their turn better spread along the second and the third variate (plot of discriminant score 1 vs 2 in fig.1).

By evaluation of the Mahalanobis distances between groups, a significant (P>95%) separation among the varieties was achieved, except for 18 variety categories allocated in three groups of 2 categories and in one group of 12 categories. As a matter of fact, two of the three smallest groups referred to clones of Morio Muskat and Muscat d'Alexandrie (or Muscat de Setubal), respectively, while the other referred to the Muskat x Trollinger and Trollinger x Muscat d'Alexandrie crossbreeds with different skin colour. The 12 varieties of the forth group, 11 of them being the same as those grouped in an indistinct group by cluster analysis, included Red, Rose and White Muscats (i.e. Muscatel do Douro, Gelb Muscat 63/2, Muscat d'Alsace blanc, Moscato Rosso, Muscat Rosé, Muscatel Roxo, the three Roter Muskateller, both Muscat à petits grains and Muscat belji) resulting very similar to one another by profile comparison: this group could be defined as that of Muscat à petits grains-type varieties. The Muscat belji resulted well separed from the other 11 varieties by considering some more variables.

We tried also to perform an unsupervised treatment of the data by the PCA analysis by using the same 12 variables, each one approached to a normal scaling of the values through a logarithmic transformation. The aim was to reduce the dimensionality of the original system, but retaining an important part of information that can be easily explained. The first two eigenvectors (82 % of the total variance) contained useful information to discriminate among single varieties, but also among groups of varieties defined on the basis of some practical indications from the profile characteristics. In order to make easier the visualization of some results from PCA data treatment, it proved very useful to indicate with the same label the varieties arbitrarily grouped (fig. 2). This is due to many different reasons: i) a common Rhine Riesling-type profile; ii) a very poor content in monoterpenes; iii and iv) very high values of the ratio between free geraniol and linalool or, vice versa, very low values of such ratio and, at the same time, high contents of total free terpenes, v) values of the cited ratio close to 1

and middle contents of total free terpenes, as for the 12 varieties of the group indistinct by LDA procedure and the Muscat d'Alexandrie. Two groups, i.e. Muscat Bifere and Muscat of Terracina which showed in particular a very high content of α-terpineol as above quoted, remained unassigned.

Purchasing the proposed goals of this work, we examined also the possibility to compare the aroma profiles of the considered Muscat-called varieties with those of other varieties or clones with Muscat-floral scent as for presumed Chardonnay mutations, called Chardonnay musqué. Thus, the mentioned PCA data treatment procedure for the same variables was also applied including the analytical results of Chardonnay musqué grape samples from single vines and referred to the same vintage. The group scores on the plane of the first two eigenvectors, evidenced their common allocation in a space free from the other categories, allowing a good singling out possibility. Moreover, the distances between this group and the Muscat groups were not higher than those between the Muscat groups.

Finally, as a possible, even if not exhaustive, useful summarizing display method of some interesting information derived by fitting intuitive deductions with objective mathematical confirmations, we reported in fig. 3 some of the more typical aroma profile typologies - on the basis of the mean values of 10 compounds under both forms, including the variables selected by statistical methods - for the groups separed also by LDA or PCA data treatment procedures, emphasyzing clear differences among themselves. In particular, the ratios between geraniol and nerol, as well as between hodiendiol (1) and (2) seem to play an important role in a differentiation within some Muscats, as between the Muscat a petits grains-typology and that of Muscat d'Alexandrie.

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Supplementary material available: Tables or diskette reporting the data set of the variables considered for all the grape samples are supplied on request.

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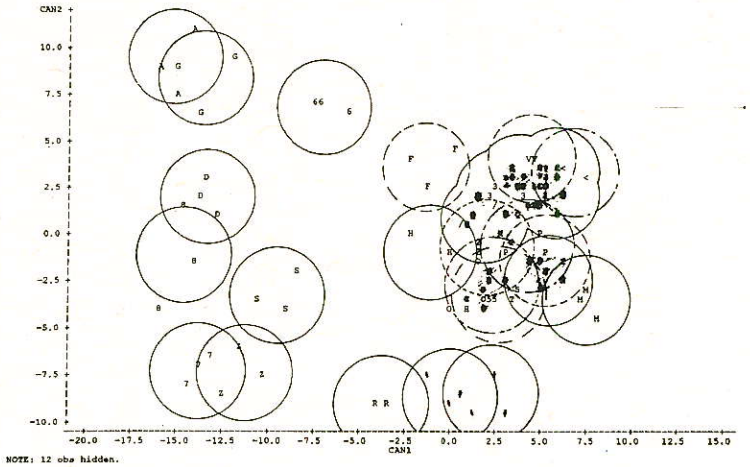


Figure 1 : Muscat groups data set : plot of discriminant score 1 vs 2 (LDA by using 12 variables selected dby stepwise procedure)

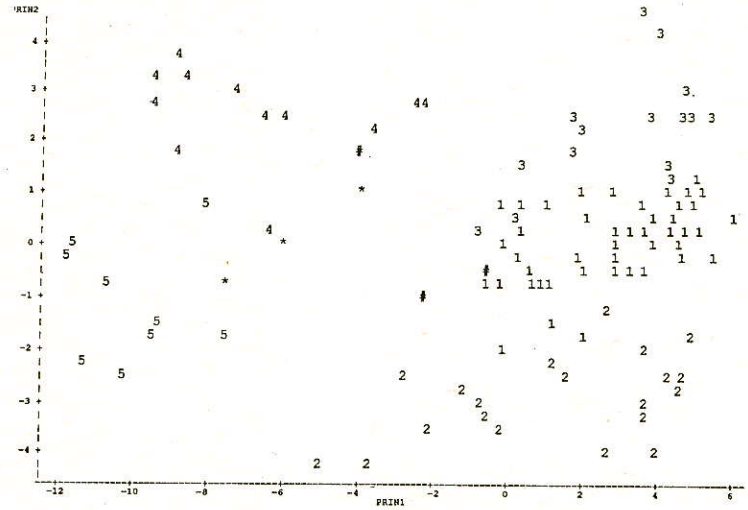
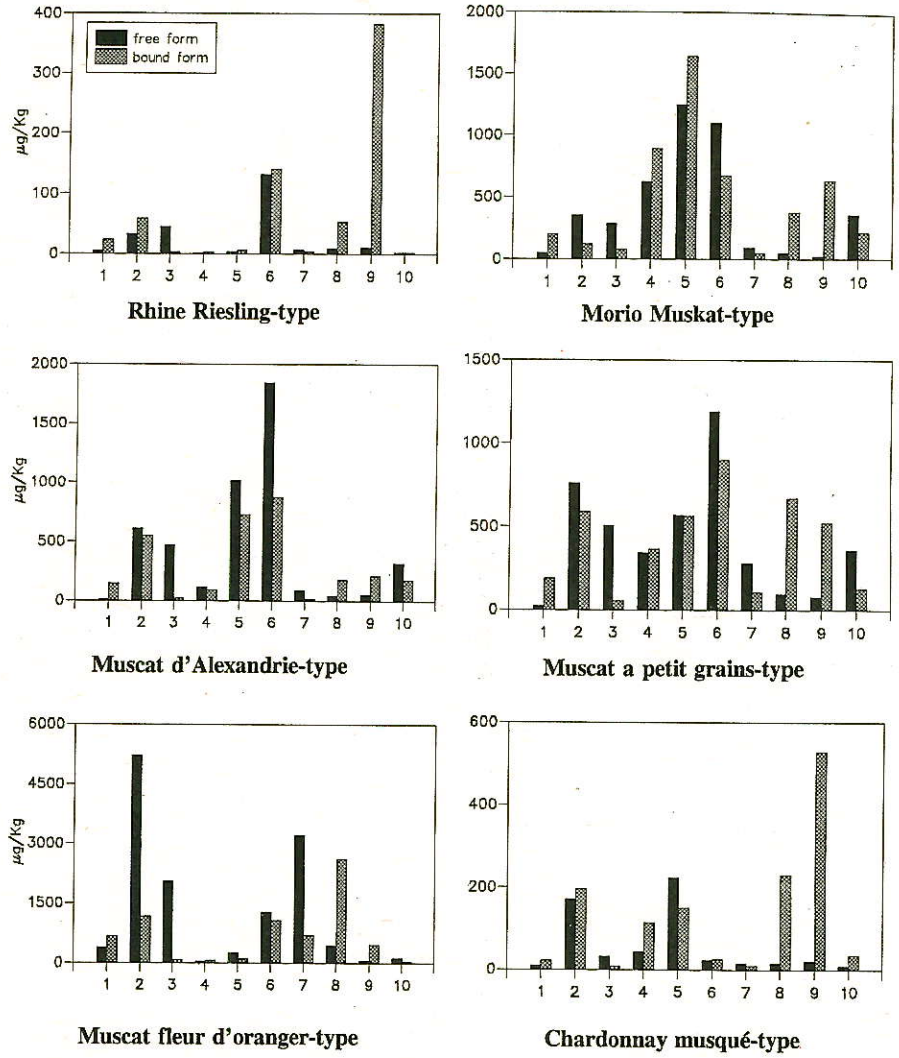


Figure 2 : Data set muscats : scores with arbitrary label assignment



1. tr. f. linal. oxide; **2.** linalool; **3.** tr. p. linal. oxide; **4.** nerol; **5.** geraniol; **6.** HO-diendiol(I); **7.** HO-diendiol(II); **8.** tr. 8-OH-linalool; **9.** cis 8-OH-linalool; **10.** 7-OH-geraniol.

Figure 3 : Examples of aroma profiles of Muscat-called varieties.