Flavour compounds of clones from different grape varieties

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Summary: The selection of highly productive and characteristic clones is essential for the maintenance and improvement of the viticultural and commercially valuable qualities of certain grape varieties. In the future, this very difficult and time consuming selection of adapted clones will be supplemented with more precise analytical techniques. In this regard, GC analysis will be most valuable.

Analytically, German white wines can be divided into three groups by the content of only a few monoterpene compounds ('terpene profiles'): 'Riesling', 'Muscat' and 'Sylvaner' or 'Weißburgunder' types. Furthermore, the use of linear discriminant analysis on some components allows the differentiation within types (e. g. for 'Riesling'-tpye: Riesling, Müller-Thurgau, Bacchus, Kerner, Ehrenfelser, Scheurebe).

Till now no significant differentiation could be made from flavour compounds of Riesling clones, although clear differences can be perceived between wines from Traminer clones. Wines with a low sensory appraisal typically have a low content of monoterpene compounds.

Differences can also be recognized in the aroma profiles of Chardonnay clones, allowing an analytical differentiation between aromatic and non-aromatic types. Certain clones, however, show differing compositions of flavour compounds when grown in different areas (clones with an 'unstable' aromatic character).

Also during ripening of the berries, differences occur within individual Chardonnay clones, resulting in a few clones having recognizable ripening curves for monoterpene compounds.

Key words: must, wine, flavour, terpene, analysis, sensory rating, statistics, selection, clone, variety of vine, Germany, Italy.

For enological and economic reasons, the selection of productive clones with a typical varietal aroma is of considerable importance to keep and improve the good qualities of a grape variety.

The aim of our investigations is to support the difficult and lengthy procedure of clone selection, involving must and wine quality evaluations, by reproducible analytical methods.

To judge the varietal character of musts and wines GC analysis should provide important informations. Some aspects concerning the successful analytical differentiation of grape and wine varieties are:

- a complete enrichment of the aroma compounds without artefacts
- a complete and quantitatively reproducible separation of the aroma compounds
- and it is especially necessary to determine 'key substances'; these are substances which occur in very different concentrations correlating to a single variety.

Monoterpenes are well-known to play an important role in the characterization of wine varieties (Rapp 1988). At present, about 50 monoterpene compounds can be identified in must and wine. Based on quantitative data from only 12 monoterpenes, German white wines can be divided into three groups: the 'Muscat group', the 'Riesling group', and the 'Silvaner-Weißburgunder group'. In the terpene patterns ('terpene profiles') clear differences exist between the varieties with a Muscat-related aroma, those with a fruity Riesling-related aroma and those with a neutral bouquet (Rapp 1982; Rapp *et al.* 1983; Rapp and Mandery 1986; Rapp 1988).

Application of statistic methods to the analytical data, as for example discriminant analysis, allows a clear differentiation of wine varieties. Wines of the varieties Riesling, Müller-Thurgau and Silvaner could be separated with the content of a few monoterpene compounds (Rapp and Güntert 1985; Rapp 1988). In recent investigations, we could even differentiate Riesling, Ehrenfelser, Kerner, Bacchus and Scheurebe, which all derive from Riesling and often exhibit similar bouquets.

Considering these results, it is also likely that wines of the same variety but of different clones can be characterized by means of GC analysis.

Comparing the terpene patterns of several Riesling clones – all grown at the same location and treated equally – we could not find any significant difference (Fig. 1). Furthermore, no

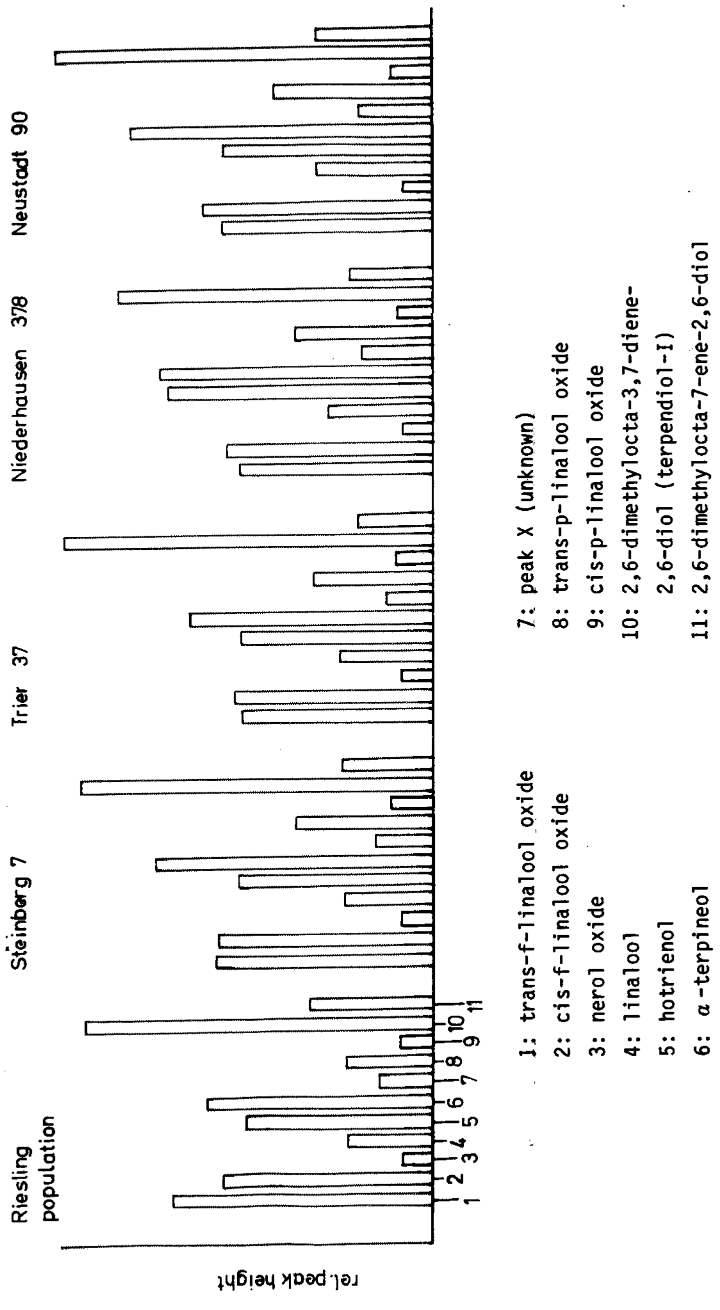


Fig. 1: 'Terpene profiles' of several Riesling clones.

significant correlations exist between terpene concentrations and sensory differences. Evaluation of the complete analytical data revealed that compounds other than monoterpenes showed

Table 1: Monoterpene compounds (relative peak height) of different Traminer clones (LLFA Neustadt, 1987)

	FR 46-107	N 23	N 25	N 22	Gm 1	K 33	Lb 14	C 48
trans-f-linalooloxide	63	61	201	203	219	186	243	216
linalool	341	367	947	894	814	995	1336	965
α -terpineol	166	160	435	407	377	477	585	483
citronellol	79	99	279	272	219	314	284	216
nerol	43	53	242	226	176	232	216	148
2,6-dimethylocta-3,7-diene-2,6-diol	63	34	248	215	219	232	239	185
rank: first place / last place	- / 13	3 / 13					15 / -	

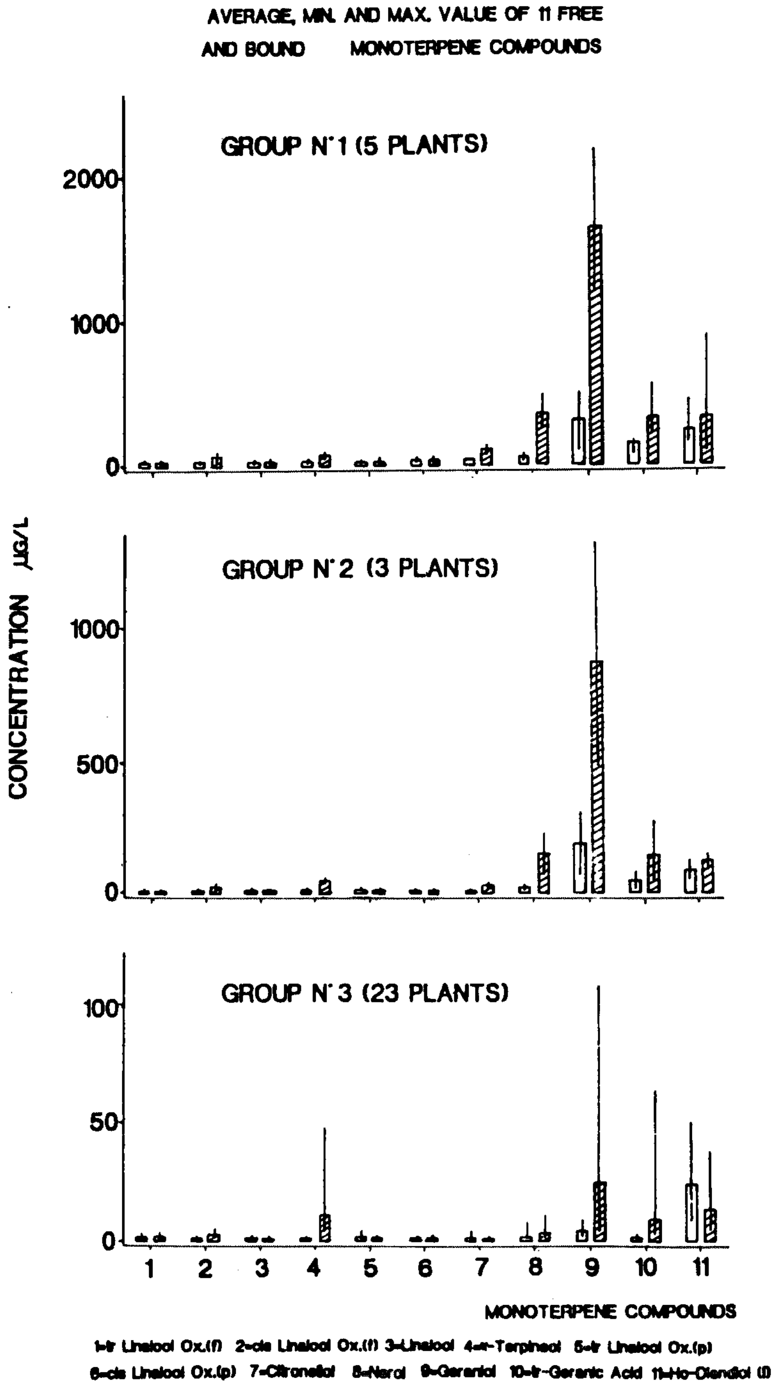


Fig. 2: 'Terpene profiles' from musts of 3 Traminer vines groups (Trentino, vintage 1987). The groupe were detected by cluster analysis.

Table 2: Gewürztraminer wines (1985 and 1986): Linear correlations between score evaluation and concentration of some monoterpene compounds

Compound		Coefficient	
nerol	smell	0.4841	0.040
nerol	taste	0.8681	0.000
geraniol	smell	0.8041	0.000
geraniol	taste	0.6237	0.009
linalool	smell	0.2450	0.199
linalool	taste	0.1323	0.326

differences between the various Riesling wines. Basically, the components concerned are fermentation compounds which can influence the wine bouquet. Hence it is not possible to judge the varietal character of the different Riesling clones tested (VOLKMANN 1989).

In further investigations, the aroma compounds – especially monoterpenes – of 8 Traminer clones were determined. Table 1 shows clearly that analytical and sensory data are well correlated. In sensory evaluation, the clone Lb 14 received a first place ranking 15 times, the clone FR-46-107 received a last place ranking 13 times. In accordance with these sensory results, the monoterpene concentrations of clone Lb 14 are very high, while those of clone FR-46-107 are low. It could be shown that clones with a typical Traminer aroma have higher geraniol and nerol concentrations than less aromatic clones (VOLKMANN 1989). For these monoterpenes, high correlation coefficients up to 0.9 between score evaluation and terpene concentration were calculated (Table 2) (AURICH *et al.* 1989).

Using the results of these investigations, we tried to identify various types of Traminer clones out of a population by analysing the aroma composition of the musts. This population was an unknown mixture of different clones of French origin. Free and bound terpene concentrations of these musts harvested from 31 plants were determined. The analysis was carried out at comparable degree of ripeness and each time under the same conditions.

The results show clear differences between the monoterpene concentrations whereas the 'terpene profiles' are comparable. Based on the quantitative data of 11 monoterpene compounds and on cluster analysis, two aromatic groups with 5 and 3 plants, and one neutral group with 23 plants were found. The terpene concentrations in the aromatic groups were about 10 times higher than in the neutral group no. 3 (Fig. 2).

We then compared the population of unknown clones with the analytical data (Fig. 3) of some Traminer clones known to have ampelographic and sensory differences. Savagnin clones, for instance, are known as Traminer clones with only slight aromatic flavour properties, whereas Gewürztraminer is much more aromatic.

Discriminant analysis of unknown and known clones together – that means that a function was calculated to differentiate the three groups of unknown clones and the same function was used for the Savagnin and Gewürztraminer clones – revealed that the Savagnin clones belonged to one of the clustered groups of unknown neutral clones and the Gewürztraminer clones should be classified into the aromatic group (Fig. 4).

It can be concluded that a characterization of Traminer clones based on the analytical data of a number of monoterpene compounds is possible.

Chardonnay clones also possess different sensory characteristics. They range between neutral, as for example the clones 116 and 130 SMA, and quite aromatic, as for example the Chardonnay clones Musqué and 77. An analytical differentiation should be possible.

The results of GC analysis (Table 3) actually showed that there were significant differences between the monoterpene concentrations of aromatic and less aromatic clones (Versini *et al.* 1988). Table 3 refers to certain Chardonnay clonal grapes from Trentino. The relatively high contents of (E)- and (Z)-2,6-dimethyl-octa-2,7-diene-1,6-diol have to be pointed out especially in bound forms and even in clones defined as 'neutral', such as the 130 SMA and 116. Usually the amount of the (Z)-compound was larger than that of (E).

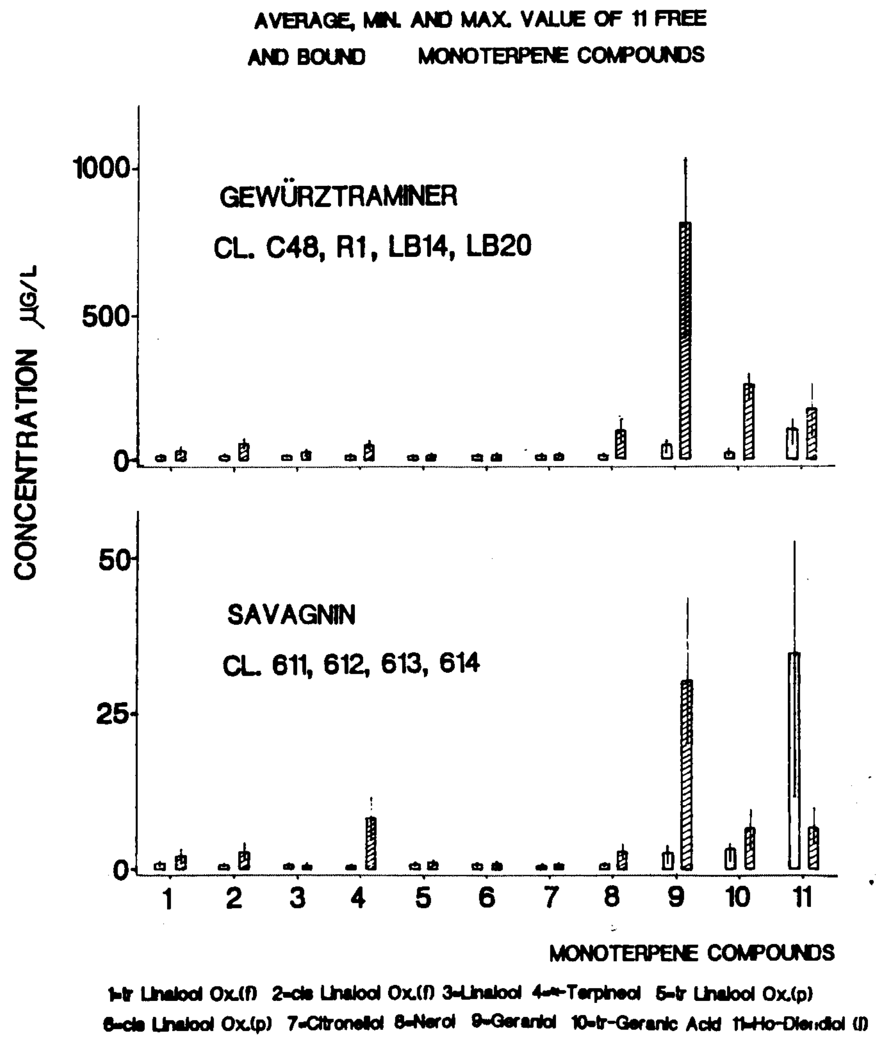


Fig. 3: 'Terpene profiles' from musts of Gewürztraminer and Savagnin clones (Trentino, vintage 1988).

Again a population of unknown clones (18 plants) was taken and the concentrations of free and bound monoterpenes in the grapes were determined. One neutral and two aromatic groups were found by cluster analysis. The monoterpene concentrations of the aromatic groups B and C were about 10 times higher than those of the neutral group A. Again a clear correlation between terpene contents and aromatic flavour can be seen (Fig. 5).

To characterize different clones by analytical methods it is necessary to use only those aromatic compounds which depend as little as possible on vintage. Investigations on the dependence of the evolution of free and bound monoterpene concentrations on the degree of ripeness were carried out over 3 years with Chardonnay clones. The contents of monoterpene compounds were analysed several times during the ripening period (VERSINI *et al.* 1989).

Fig. 6 shows that the content of free trans-pyranoid-linalooloxide in the more aromatic clone 77 is much higher than in the neutral clone (130 SMA), but the shapes of the curves are comparable. There is an increase at the beginning of the ripening period and a decrease after a certain time. Also the linalool concentrations (Fig. 7) are much higher in the aromatic clone 77 than in the more neutral clones (130 SMA, 116). Evaluation of linalool showed differing tendencies between clones. For the neutral clone 130 SMA, the concentrations of free and bound linalool

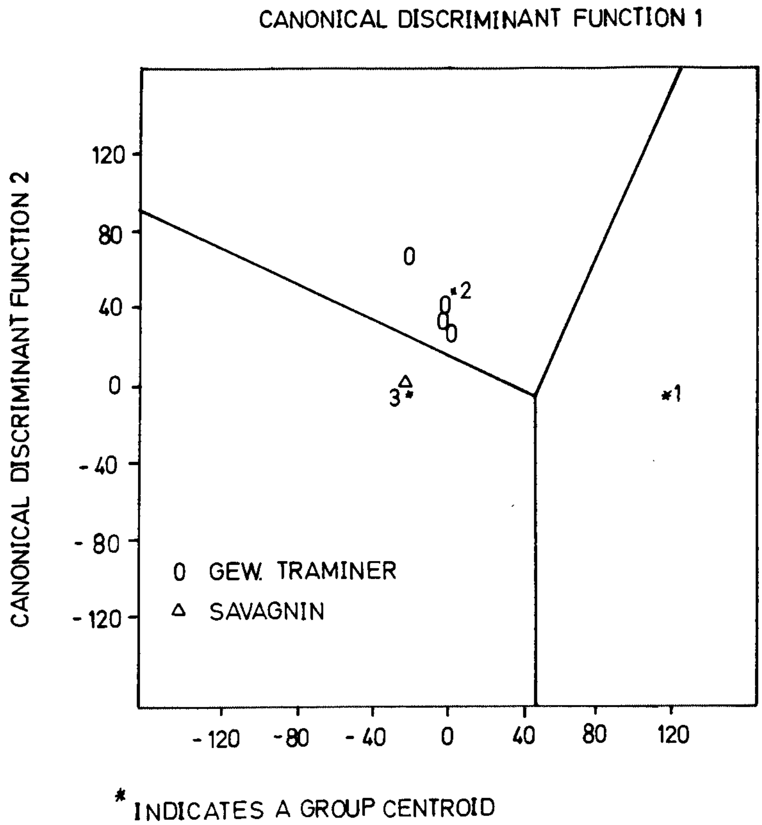
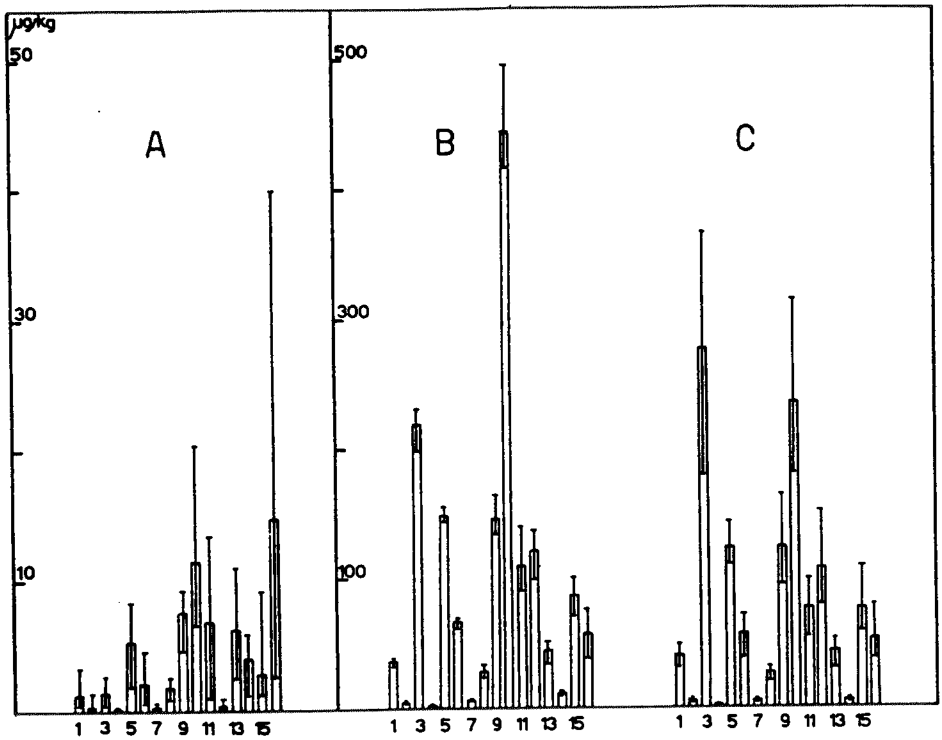


Fig. 4: Discriminant analytical differentiation of 31 Traminer plants in 3 groups, fixed by clustering, using 11 free and bound monoterpene compounds. Inside classification of clonal Gewürztraminer (0) and Savagnin (Δ).

Table 3: Free (f) and bound (b) components ($\mu g/kg$ of berries) in Chardonnay grapes (Trentino 1986)

Compounds	Clone Musqué 9-9-'86		Clone 77 12-9-'86		Clone 130 SMA 9-9-'86		Clone 116 9-9-'86	
	(f)	(b)	(f)	(b)	(f)	(b)	(f)	(b)
trans-f-linalooloxide	11	26	3	26	7.5	1.9	54	2.0
cis-f-linalooloxide	2.7	2.0	0.5	1.3	0.4	0.3	4	0.3
linalool	40	383	137	123	1.6	4	3	17
trans-p-linalooloxide	36	6.5	85	5.5	3.9	0.7	1.2	0.3
cis-p-linalooloxide	12	3.1	31	1.3	0.9	0.3	0.5	0.2
nerol	87	67	12.5	10	2.6	7	2.2	2.8
geraniol	325	114	49	19	14	13	9	6
2,6-dimethylocta-1,7-diene-3,6-diol	181	36	221	24	-	-	-	-
(E)-2,6-dimethylocta-2,7-diene-1,6-diol	84	334	108	264	15	72	11	62
(Z)-2,6-dimethylocta-2,7-diene-1,6-diol	535	976	85	258	85	400	83	208
nor-isoprenic dicetone	-	36	-	26	-	70	-	40
3-oxo-α-ionol	-	424	-	200	-	640	-	313
2-phenylethanol	550	77	525	243	622	222	732	93

increase during the ripening period. The aromatic Chardonnay clone 77 shows maxima of linalool concentrations, after which the curves of free and bound linalool decrease to very low concentrations. These tendencies were observed in all 3 years.



A: 'Neutral' 9 plants; B: 'Aromatic' 3 plants; C: 'Aromatic' 6 plants.

Considered compounds:

1: tr-furan linalool oxide	9: geraniol
2: cis-furan linalool oxide	10: tr-geranic acid
3: linalool	11: ho-diendiol (I)
4: α-terpineol	12: ho-diendiol (II)
5: tr-pyran linalool oxide	13: 8-hydroxy-6.7-dihydrolinalool
6: cis-pyran linalool oxide	14: 7-hydroxycitronellol
7: citronellol	15: tr 8-hydroxylinalool
8: nerol	16: cis 8-hydroxylinalool

Fig. 5: 'Terpene profiles' of 3 groups of Chardonnay determined by clustering. Average minimum and maximum concentrations of free monoterpene compounds. - A: Neutral group (9 plants), B: aromatic group I (3 plants), C: aromatic group II (6 plants).

The results show that an analytical characterization based on monoterpene compounds is also possible for different Traminer and Chardonnay clones, but not for the Riesling clones which

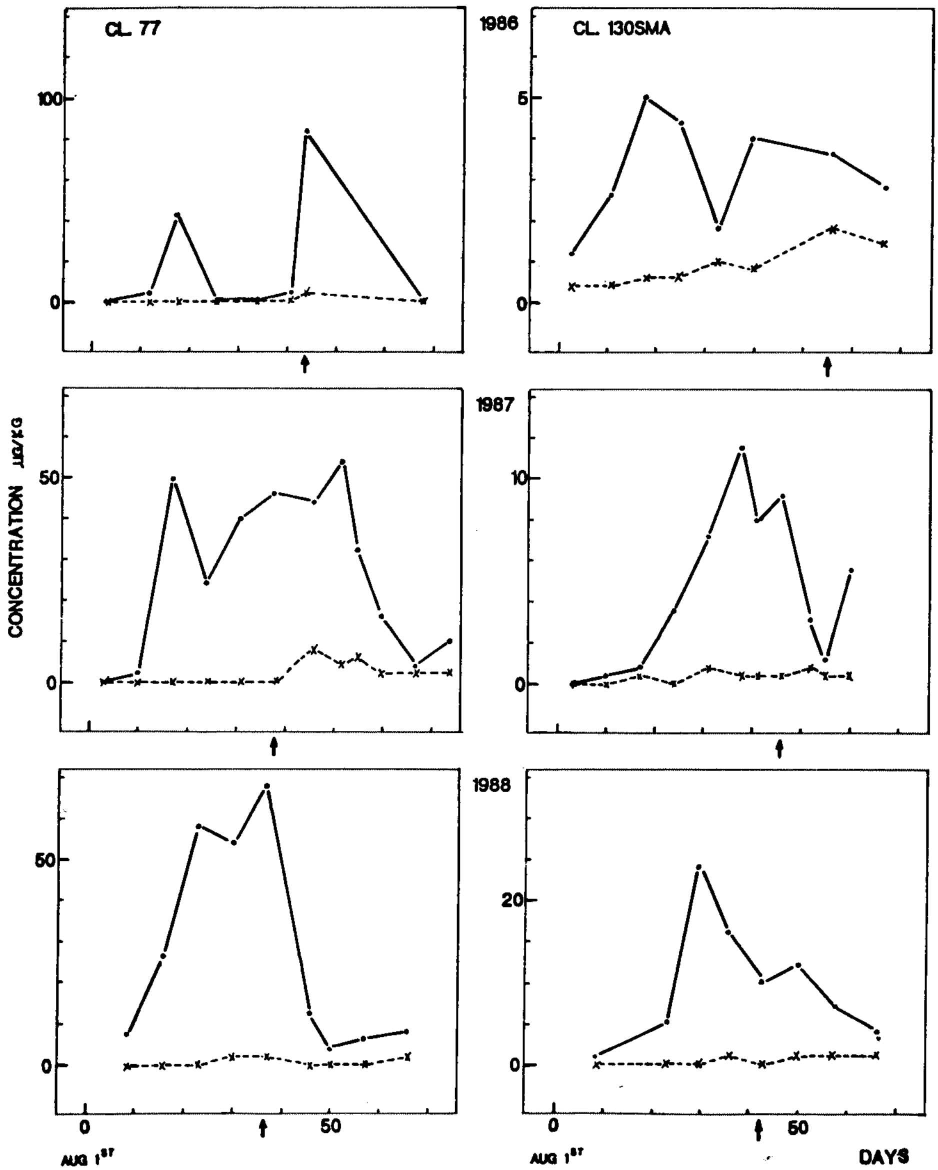


Fig. 6: Chardonnay clones: Evaluation of trans-pyranoid-linalool-oxide during ripening (free = full line, bound = broken line).

have been investigated. For an accurate characterization, the GC analysis should be carried out at comparable degrees of ripeness.

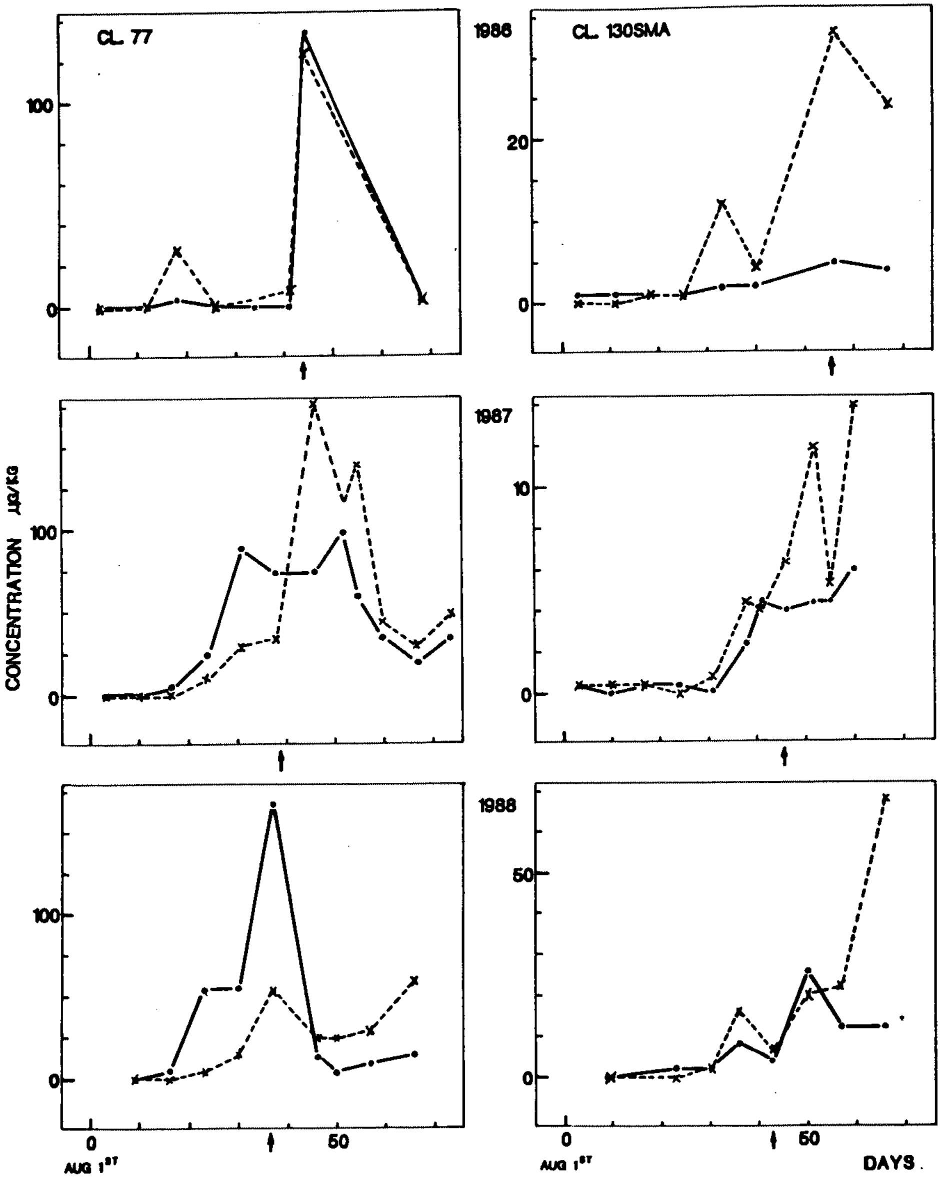


Fig. 7: Chardonnay clones: Evaluation of linalool during ripening (free = full line, bound = broken line).

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