VOLATILE COMPOUNDS IN GRAPES AND WINES FROM TWO MUSCAT VARIETIES CULTIVATED IN GREEK ISLANDS

COMPOSÉS VOLATILS DE RAISINS ET DE VINS ISSUS DE DEUX CÉPAGES MUSCAT CULTIVÉS DANS DES ÎLES GRECQUES

P. LANARIDIS*, Marie-Jeanne SALAHA, Irini TZOUROU, E. TSOUTSOURAS and S. KARAGIANNIS

Wine Institute of Athens, National Agricultural Research Foundation, 1 Sofokli Venizelou str., Lykovrissi 14123, Grèce

Abstract: The concentrations of free and glycosidically linked monoterpenes and volatile alcohols in grapes and wines from the cultivars Muscat lefko and Muscat of Alexandria, cultivated in the islands of Samos and Lemnos respectively, were determined. The relationship between free and linked monoterpenes in grapes and wines as well as the relationship between grapes and wines in their monoterpene content was investigated, showing some differences between the two cultivars and the different vineyards. It is also demonstrated that skin-contact for 8 h at a temperature up to 15 °C, resulted in marked increases in the concentrations of free and linked monoterpenes in wines from both Muscat cultivars.

Résumé : Les concentrations des monoterpènes libres et glycosylés dans des raisins et les vins correspondants issus des cépages Muscat lefko et Muscat d'Alexandrie cultivés dans les îles grecques de Samos et de Lemnos, ont été déterminées. On a mesuré les concentrations de l'alcool benzylique, de phényl-2-éthanol et des alcools en C6, libres et glycosylés. L'extraction des composants libres et glycosylés des jus de raisins et des vins a été réalisée à l'aide d'un adsorbant (C18) et de différents solvants. Cette technique permet d'isoler et de séparer les fractions libres et glycosylées de l'arôme. La première fraction est analysée directement par chromatographie en phase gazeuse couplée à la spectrométrie de masse (CPG-SM). La seconde fraction est analysée par CPG-SM après une hydrolyse enzymatique libérant les aglycones volatils. L'étude a montré que les raisins des cépages Muscat lefko et Muscat d'Alexandrie sont riches en monoterpènes. Néanmoins, les raisins de Muscat d'Alexandrie renferment des concentrations inférieures en monoterpènes par rapport à celles de Muscat lefko. Les concentrations des alcools non terpéniques ne présentent pas de différences importantes dans les raisins des deux cépages. Pour les deux cépages, la part de linalool, nérol et géraniol sous forme glycosylée est nettement plus abondante que la part libre dans les raisins. Quel que soit le cépage, la part de linalool sous forme libre est supérieure à la part de linalool sous forme de glycoside dans les vins. Au contraire, la majorité de la quantité de nérol et de géraniol se trouve sous forme des glycosides dans les vins des cépages examinés. Les vins de Muscat d'Alexandrie conservent la majorité (47 - 87 p. cent) du potentiel aromatique des raisins tandis que les vins de Muscat lefko contiennent un pourcentage de 36 à 68 p. cent de la quantité des monoterpènes des raisins. En ce qui concerne les traitements préfermentaires des raisins, la macération pelliculaire (8 heures à T≤15 °C) conduit à des teneurs plus élevées en monoterpènes libres et glycosylés dans les vins correspondants, pour les deux cépages.

Key words: free monoterpenes, glycosidically linked monoterpenes, maceration, Muscat cultivars, Greek wines.

Mots clés : monoterpènes libres, monoterpènes glycosylés, macération, cépages Muscats, vins grecs.

INTRODUCTION

Aromatic typicity of a wine is mainly attributed to constituents characteristic of the grape cultivar, flavour compounds found in grapes prior to fermentation under a volatile and non volatile form. Monoterpenes are among the most important aromatic compounds found in grapes and giving wine a specific character (RIBÉREAU-GAYON *et al.*, 1975; MARAIS, 1983; GÜNATA *et al.*, 1985; WILSON *et al.*, 1986; MARAIS, 1987; BAYONOVE, 1992). Together with C13 norisoprenoids (RAZUNGLES *et al.*, 1993) monoterpenes are important compounds for the enhancement of the typicity of Muscat wines in spite of the very important presence of volatile compounds produced during alcoholic fermentation. The latter are not characteristic of the vine variety and they account for the vinous character common to all wines (BAYONOVE,

*Correspondance : wineinst@otenet.gr

J. Int. Sci. Vigne Vin, 2002, **36**, n°1, 39-47
©Vigne et Vin Publications Internationales (Bordeaux, France)

1992). Benzene derivatives (benzyl alcohol, vanillin, 2-phenylethanol), together with C6 alcohols (hexanols and hexenols, responsible for herbaceous character) are also a group of volatile compounds originating from grapes (CORDONNIER and BAYONOVE, 1981; SEFTON *et al.*, 1993).

Varietal aroma depends mainly on cultivar but is also influenced by altitude, soil, climate and viticulture practices contributing to its intensity (WILSON *et al.*, 1984; DI STEFANO and CORINO, 1986; REYNOLDS and WARDLE, 1997; SALAHA *et al.*, 1999). This typical and original aroma is due in a part to volatile compounds issued from grapes and depends on whether they are in free or combined form. Another part of varietal aroma is due to non volatile compounds revealed during vinification or ageing of wines OLIVEIRA *et al.*, 1999).

The vine varieties Muscat lefko and Muscat of Alexandria are cultivated in the Greek islands of Samos and Lemnos respectively and produce famous dessert wines deserving appellations of origin. In the present work our aim was to elucidate the evolution of monoterpenes during winemaking in order to improve the vinification techniques and to enhance the quality of the wines produced in these islands.

As Muscat cultivars are considered to be models for the study of flavour compounds, due to their aromatic abundance (GÜNATA, 1994), a research programme, based on the determination of varietal aroma and the factors affecting it, in both grapes and wines, was established; vineyards were selected in both islands, with the collaboration of the local wineries. The winemaking technique of skin-contact was used as an effective means for the extraction of additional aroma compounds, such as monoterpenes, from grape skins during wine production.

This paper deals with the investigation of several monoterpenes in grapes and wines of the cultivars Muscat lefko and Muscat of Alexandria, the relationship between the free and glycosidically linked fraction, the degree of their extraction from grapes to wine, as well as the impact of skin-contact technique on wine quality. Also, the levels of some free and glycosidically linked volatile alcohols are determined.

MATERIALS AND METHODS

I - EXPERIMENTAL VINEYARDS

Vineyards from different areas of the islands were selected in order to determine a representative range of concentrations of monoterpenes and alcohols of the two cultivars. The characteristics of the vineyards and the crop level are given in table I. In both islands the training system was the goblet. Grapes (130 - 170 kg per vineyard) were harvested at potential alcohol content 13.5 - 16.0 p. cent at the date chosen by the vine grower, according to the altitude of the vineyard. Clusters with appreciable mold or other damage were discarded during selection. Berry samples were randomly selected and immediately frozen (-20 °C) until required for analysis.

II - FERMENTATION CONDITIONS

The grapes were hand picked from both Muscat cultivars and were destemmed, crushed and then pres-

TABLE I
Experimental vineyards
Vignobles expérimentaux

	Vineyard	Altitude (m)	Age (years)	Yield (kg of grapes/ha)		Dates of harvest	
				1997	1998	1997	1998
Muscat lefko (Island of Samos)	1	10	25	20000	21000	15/9	31/8
	2	20	25	18000	17500	3/9	21/8
	3	50	15	15000	16500	19/8	17/8
	4	200	25	15000	15000	3/9	27/8
	5	300	30	5000	6000	6/10	1/10
	6	400	20	7000	6000	17/9	4/9
	7	530	15	9000	8000	1/10	29/9
	8	650	20	7500	7500	7/10	25/9
	9	650	17	7500	7000	9/10	25/9
Muscat of Alexandria (Island of Lemnos)	1	15	35	8000	6500	5/10	10/9
	2	20	10	14000	15000	5/10	10/9
	3	50	23	10000	9000	21/9	10/9
	4	250	15	20000	21000	10/10	27/9

©Vigne et Vin Publications Internationales (Bordeaux, France)

sed in discontinuous horizontal press. The resultant juices (free run combined with the first two pressings) were sulfited at 80 mg/L, allowed to settle at 3 °C for 24 hours and racked. Their fermentation was conducted at controlled temperature (18 - 20 °C) in stainless steel tanks. Half of the quantity of the grapes harvested from some vineyards was crushed and left to skin contact of 8 h at a temperature not exceeding 15 °C before pressing. All fermentations were conducted in the presence of a commercial yeast strain of *Saccharomyces cerevisiae* (Fermivin Cryo, Gist-brocades, France) at 20 g/hL. At the completion of fermentations, the resultant wines were racked, filtered and stored at 0 °C for 1 month before analysis. Measurements of alcohol content, residual sugars, volatile acidity, total acidity and pH were carried out according to the OIV methods (OIV, 1990) and are given in table II.

III - GRAPE AND WINE ANALYSIS

Analysis was not realized later than 3 months following berry collection. Berries were crushed and mixed in a blender at 0 °C. The homogenate was filtered through a gauze and centrifuged at 16,000 g at 0 °C for 15 min. Analyses of free and glycosidically linked monoterpenes as well as alcohols (1-hexanol, hexenols, benzyl alcohol and 2-phenyl ethanol) were carried out by the method of DI STEFANO (1991). A sample of 25 mL of centrifuged grape juice or wine and 0.1 mL 1-octanol 19.4 mg/L (internal standard) were added to 25 mL deionized water. The mixture was then passed under suction (flow 5 mL/min) through a SPE column containing 1 g C-18 (IST Ltd, UK) already activated with 10 mL CH_3OH and then 20 mL H_2O. The hydrophilic compounds were eliminated by addition of 20 mL H_2O. Extraction of free, mono- and di-hydroxylated monoterpenes was done with 35 mL CH_2Cl_2. The extract was dried over Na_2SO_4 and the solvent was removed up to 1 mL by distillation through a Vigreux column. Two microliters of the sample were injected to the GC/MS for analysis. Extraction of trihydroxylated and glycosidically linked monoterpenes was achieved with 30 mL CH_3OH. The solvent was removed in a rotary evaporator (25 °C - 30 °C) and then 3 mL of phosphate-citrate buffer pH 5 (0.1 M) were added as well as 70 mg of the β-glycosidase enzyme Novoferm 12 G (Novo Nordisk Ferment Ltd, Dittingen, Switzerland). The enzyme was allowed to react for 24 hours at 37 °C. After addition of 0.1 mL of the internal standard, the free monoterpenes released were extracted with 30 mL CH_2Cl_2 , as recommended by the analytical method used. The solvent was then removed, as described above, to a final volume of 1 mL. 2 µL of the sample were injected to the GC/MS for analysis. The GC-MS unit consisted of a Hewlett Packard 6890 gas chromatograph coupled to a HP 5972 mass selective detector. The GC was equipped with a Hewlett Packard 25 m x 0.2 mm x 0.2 µm Innowax (crosslinked polyethylene glycol) capillary column (HP, USA). Splitless mode was used. The chromatographic conditions were as follows: initial temperature, 60 °C for 5 min and then ramped at a rate of 1.5 °C/min to 140 °C and at 3 °C/min to 205 °C using helium as the carrier gas (column head pressure: 18

TABLE II
Conventional analyses of wines
Analyses conventionnelles des vins

Vineyard		Alcohol content (% vol.)	Residual sugars (g/L)	Volatile acidity (g/L)	Total acidity (g/L)	pH	Alcohol content (% vol.)	Residual sugars (g/L)	Volatile acidity (g/L)	Total acidity (g/L)	pH
				1997					1998		
Muscat lefko (Samos)	1	13.5	1.4	0.22	6.5	3.03	14.1	2.3	0.65	4.8	3.62
	2	13.7	1.4	0.17	6.3	3.01	15.4	9.3	0.41	4.7	3.58
	3	13.5	2.0	0.23	6.8	3.01	13.3	2.3	0.36	5.1	3.65
	4	14.4	1.9	0.22	6.0	3.08	15.0	8.2	0.55	5.4	3.33
	5	13.6	2.0	0.25	6.8	2.97	12.7	1.5	0.27	7.9	3.05
	6	14.6	2.9	0.49	6.9	2.98	15.6	8.3	0.60	4.8	3.43
	7	15.6	8.6	0.30	7.7	3.08	16.5	6.5	0.38	5.8	3.62
	8	15.6	7.1	0.43	6.8	3.00	15.1	7.1	0.34	5.3	3.66
	9	14.7	11.1	0.25	6.0	3.38	15.1	8.1	0.34	5.9	3.40
Muscat of Alexandria (Lemnos)	1	15.1	1.2	0.37	4.6	3.76	16.4	12.7	0.60	5.3	3.80
	2	15.1	14.2	0.76	5.1	3.74	14.1	4.0	0.52	4.8	3.83
	3	14.5	1.3	0.50	6.0	3.34	16.0	17.7	0.80	6.7	3.79
	4	16.2	17.4	0.72	5.1	3.75	15.5	7.0	0.50	6.0	3.81

©Vigne et Vin Publications Internationales (Bordeaux, France)

psi, flow rate: 1 mL/min). The injector and transfer line temperatures were held at 200 and 280 °C, respectively. Identification of compounds was accomplished by comparing retention times and mass spectra (SCAN) made with reference standards. Quantitative analysis was carried out by the use of Selective Ion Monitoring (SIM) mode. All analyses were done in duplicate and mean values are given in tables.

RESULTS AND DISCUSSION

Table III shows the range of concentrations of monoterpenes, benzene derivatives and C6 alcohols in grapes of Muscat lefko cultivar from the island of Samos and Muscat of Alexandria cultivar from the island of Lemnos. Table IV shows the same data for the correspondent wines.

I - GRAPE COMPONENTS

The levels of free linalool are higher in Muscat lefko grapes (small berries) than those of Muscat of Alexandria (large berries) in both years. On the other hand the concentration of linked linalool is generally lower in Muscat lefko grapes compared to those of Muscat of Alexandria. The levels of nerol (free and linked) are higher in Muscat lefko grapes than those of Muscat of Alexandria in both years. Our results correspond with the findings of MARAIS (1983) who reported that the largest amounts of linalool are found in the case of Muscat of Alexandria and that, in general, there are proportionately higher concentrations of nerol in Muscat grapes with small berries (such as Muscat lefko) compared to those with larger berries. Geraniol concentrations are generally higher in Muscat of Alexandria grapes except the maximum free geraniol concentration, which is higher in Muscat lefko grapes in the second year. MARAIS (1983) also reported that the largest amounts of geraniol are found in Muscat of Alexandria grapes. The total sum (free and linked) of linalool, nerol and geraniol concentrations (L+N+G), considered as an important parameter for the intensity of Muscat aroma, is higher in Muscat lefko grapes than those of Muscat of Alexandria in both years (figure1).

Furthermore, the levels of free and linked citronellol and α-terpineol were higher in Muscat lefko grapes compared to Muscat of Alexandria grapes (table III). Also nerol oxide concentrations were higher in the case of Muscat lefko grapes. Interestingly, hotrienol concentrations (free and linked) were found slightly larger in Muscat lefko grapes than those of Muscat of Alexandria in the first year of the research (1997) and vice versa in the second year (1998).

In the case of alcohols, only small differences are noticed between grapes from both Muscat cultivars. Generally n-alcohols of C6 chain length are considered as undesirable whereas benzyl alcohol and 2-phenyl ethanol may cause sweet and flowery notes that could be considered as a positive characteristic for some varieties (ROCHA *et al.*, 1999).

TABLE III
Range of concentrations of monoterpenes and alcohols in grapes of Muscat lefko and Muscat of Alexandria cultivars (in µg/L).

Variation des concentrations de monoterpènes et alcools dans les raisins de cépages Muscat lefko et Muscat d'Alexandrie (en µg/L).

Compounds	1997				1998			
	Muscat lefko		Muscat of Alexandria		Muscat lefko		Muscat of Alexandria	
	Free	Linked	Free	Linked	Free	Linked	Free	Linked
Linalool	73-735	287-926	55-98	356-1342	167-643	391-1428	156-256	706-1832
Nerol	36-148	467-1549	22-50	173-531	32-370	786-1857	42-85	409-597
Geraniol	91-354	523-1615	239-401	712-2019	64-449	449-1153	208-297	554-1308
L+N+G	346-1108	1277-3952	352-549	1280-3892	346-1462	2123-3881	439-595	1669-3737
Citronellol	10-24	30-70	5-9	14-23	4-17	31-56	2-6	7-13
α-Terpineol	6-13	6-35	2-9	2-16	7-29	23-71	8-10	12-33
Nerol oxide	10-23	10-53	6-10	8-15	8-21	52-95	9-13	23-30
Hotrienol*	0.3-1.3	0.3-0.9	0.4-1.2	Tr-0.5	2.3-2.9	1.1-1.9	2.7-3.2	2.5-6.0
1-Hexanol	54-196	119-326	60-92	82-451	37-225	279-696	105-214	244-386
∑ hexenols	153-337	31-206	218-590	110-164	206-434	144-303	291-454	261-331
Benzyl alcohol	142-197	100-245	114-184	71-129	131-226	260-378	104-201	379-409
2-Phenylethanol	65-415	70-213	91-340	64-127	108-268	152-297	134-174	132-291

* Estimated with the ratio of the area of the substance to the area of the internal standard

©Vigne et Vin Publications Internationales (Bordeaux, France)

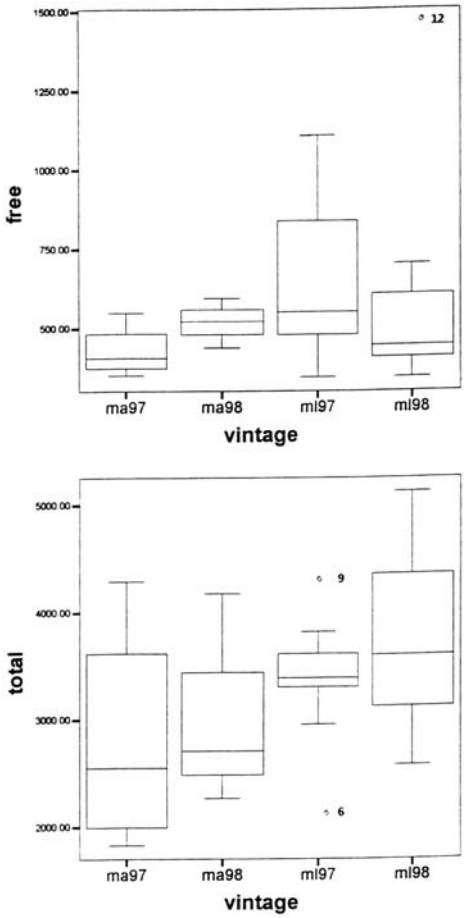


Figure 1 - (Linalool + Nerol + Geraniol) concentration in grapes
(ma: Muscat of Alexandria, ml: Muscat lefko; 97, 98: vintages).
Concentration du (Linalool + Nérol + Géraniol) dans les raisins
(ma : Muscat d'Alexandrie, ml : Muscat lefko ; 97, 98 : années de récolte)

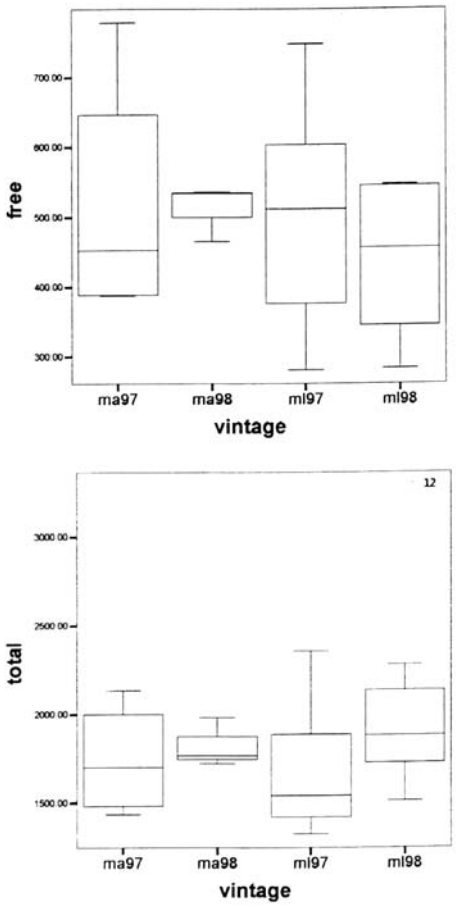


Figure 2 - (Linalool + Nerol + Geraniol) concentration in wines
(ma: Muscat of Alexandria, ml: Muscat lefko; 97, 98: vintages).
Concentration du (Linalool + Nérol + Géraniol) dans les vins
(ma : Muscat d'Alexandrie, ml : Muscat lefko ; 97, 98 : années de récolte)

TABLE IV
Range of concentrations of monoterpenes and alcohols in wines of Muscat lefko and Muscat of Alexandria cultivars (in µg/L).

Variation des concentrations de monoterpènes et alcools dans les vins de cépages Muscat lefko et Muscat d'Alexandrie (en µg/L).

Compounds	1997				1998			
	Muscat lefko		Muscat of Alexandria		Muscat lefko		Muscat of Alexandria	
	Free	Linked	Free	Linked	Free	Linked	Free	Linked
Linalool	221-575	15-575	171-644	62-388	200-419	172-295	303-408	322-507
Nerol	19-62	444-617	25-41	178-240	33-65	550-1450	32-51	254-258
Geraniol	41-111	396-813	81-178	722-1056	50-82	386-1051	96-146	613-682
L+N+G	281-748	911-1753	387-778	1044-1358	283-547	1144-2771	465-536	1189-1447
Citronellol	12-95	12-35	39-81	5-7	3-12	5-10	4-8	2-5
α-Terpineol	126-280	4-9	55-204	3-6	25-47	3-18	10-14	2-7
Nerol oxide	7-15	11-21	5-8	7-12	7-11	16-41	8-9	8-10
Hotrienol*	0.6-1.4	Tr-0.2	0.5-2.5	Tr-0.4	1.5-4.5	0.3-1.0	3.2-5.1	0.5-0.6
1-Hexanol	504-830	105-263	$(0.7\text{-}2)\times10^3$	105-200	723-1757	51-233	$(1.8\text{-}2.5)\times10^3$	111-150
∑ hexenols	59-108	72-108	134-590	60-129	19-125	59-194	451-1800	121-208
Benzyl alcohol	52-127	99-212	54-96	92-180	31-111	80-172	26-112	62-176
2-Phenylethanol	$(37\text{-}57)\times10^3$	67-159	$(41\text{-}50)\times10^3$	53-177	$(13\text{-}44)\times10^3$	55-134	$(33\text{-}42)\times10^3$	57-69

* Estimated with the ratio of the area of the substance to the area of the internal standard

©Vigne et Vin Publications Internationales (Bordeaux, France)

II - WINE COMPONENTS

The range of concentrations of free linalool in wines issued from the two Muscat cultivars (table IV) does not present big differences. Linked linalool maximum concentration is higher in Muscat lefko wines in the first year (1997), whereas it is higher in Muscat of Alexandria wines in the second year (1998). The concentrations of free nerol are approximately in the same range of values in the two cultivars, whereas linked nerol amounts were significantly higher in Muscat lefko wines than those of Muscat of Alexandria. Geraniol levels are increased in Muscat of Alexandria wines but linked geraniol maximum concentration was higher in Muscat lefko wines in the second year (1998). The linked citronellol and α-terpineol levels are higher in Muscat lefko wines but hotrienol (free and linked) is more abundant in Muscat of Alexandria wines. The distribution of the values of free and total sum of linalool, nerol, and geraniol concentrations (L+N+G) in wines is given in figure 2.

The concentrations of 1-hexanol and total hexenols are markedly higher in Muscat of Alexandria wines comparatively to Muscat lefko wines (table IV). On the other hand the concentrations of the aromatic alcohols are almost similar in both Muscat varieties.

III - RELATIONSHIP BETWEEN FREE AND GLYCOSIDICALLY LINKED MONOTERPENES

Table V illustrates the percentage of free monoterpenes to the total monoterpenes in grapes and wines from both Muscat cultivars in 1997 and 1998. The monoterpenes examined in this section were linalool, nerol and geraniol since these three compounds mainly contribute to the typical Muscat aroma, have low aroma thresholds, and they are found in levels much higher than their aroma thresholds in many cultivars (BAYONOVE, 1992). It becomes apparent that free linalool may represent a large proportion (up to 68 p. cent) of total linalool in grapes of Muscat lefko but only up to 26 p. cent in the case of Muscat of Alexandria. It is remarkable that in wines from both Muscat cultivars the major part of linalool is found in its free form, which indicates that most of the linked linalool is hydrolyzed during juice processing and alcoholic fermentation. This result is important since linalool is one of the most important aromatic terpene compounds with low aroma threshold value (100 µg/l) (RIBÉREAU-GAYON *et al.*, 1975) and odor that reminds Muscat (BERTRAND, 1994) or coriander (MARAIS, 1983).

On the other hand, free nerol represents only a small part of the total nerol in grapes of Muscat lefko (2-17 p. cent) and Muscat of Alexandria (4-22 p. cent) as well as in wines from both cultivars (3-10 and 10-19 p. cent respectively, in both years). This result indicates that glycosidically linked nerol remains the major form of nerol after alcoholic fermentation. The odor threshold of nerol has been estimated between 400 and 500 µg/l (RIBÉREAU-GAYON *et al.*, 1975) and its aroma is reminiscent of flower (MARAIS, 1983) or carrot (BERTRAND *et al.*, 1994). As in the case of nerol, the concentrations of free geraniol are much lower than those of linked geraniol in grapes from the two cultivars, especially in Muscat lefko grapes. Our findings for monoterpenes in grapes are in agreement with the studies of GÜNATA (1994) demonstrating that the amount of glycosidically bound aroma compounds is generally three to ten fold higher than the amount of the free forms mainly in several cultivars including Muscats. It was also found that total bound forms were more abundant than the total free forms in skins, pulp and juice (GÜNATA *et al.*, 1985). Free geraniol in wines represents a small part (7-19 p. cent) compared to its linked form in both Muscat varieties examined. The odor threshold of geraniol has been estimated to 130 µg/l (RIBÉREAU-GAYON *et al.*, 1975) and its odor reminds rose (BERTRAND *et al.*, 1994). The bound fraction for C6 compounds were found in very low concentrations for both varieties (BELANCIC *et al.*, 1997).

TABLE V
Free monoterpenes per total (free + linked) monoterpenes ratio (x 100) (%)
Apport (monoterpènes libres / monoterpènes libres + glycosylés) x 100 (%)

Compound	Year	Muscat lefko		Muscat of Alexandria	
		Grapes	Wines	Grapes	Wines
Linalool	1997	7-68	58-96	6-20	59-87
	1998	14-49	52-66	10-26	45-51
Nerol	1997	4-12	4-10	4-22	10-19
	1998	2-17	3-9	7-17	11-17
Geraniol	1997	7-26	7-19	13-36	7-19
	1998	8-28	7-14	13-32	12-19

©Vigne et Vin Publications Internationales (Bordeaux, France)

TABLE VI
Wine monoterpenes (free + linked) per grape monoterpenes (free + linked) ratio (x 100) (%)
Rapport (monoterpènes dans les vins/monoterpènes dans les raisins) x 100 (%)

Compound	Year	Muscat lefko	Muscat of Alexandria
Linalool	1997	28-77	60-104
	1998	40-69	45-69
Nerol	1997	31-93	46-112
	1998	39-79	45-62
Geraniol	1997	37-79	37-79
	1998	48-84	52-68
L+N+G	1997	36-67	49-87
	1998	46-68	47-76

IV - RELATIONSHIP BETWEEN GRAPES AND WINES IN THEIR MONOTERPENE CONTENT

Table VI shows the percentage of the sum of concentrations of free and linked monoterpenes in wines compared to the sum of concentrations of free and linked monoterpenes in grapes for both years of experimentation. The amounts of total linalool that pass from Muscat lefko grapes to the corresponding wines present large variations (28-77 p. cent) although the conditions of juice treatment and fermentation were the same for grapes from all experimental vineyards. In the case of Muscat of Alexandria we observe that a percentage of at least 45 p. cent of total linalool of grapes is found in the corresponding wines. Wine nerol per grape nerol ratio varies between 31 p. cent and 93 p. cent in Muscat lefko whereas the ratio for Muscat of Alexandria is 45-112 p. cent, for both years. It is clear that the major part of this monoterpene is still present in wines of this cultivar. The percentage of wine geraniol per grape geraniol is approximately the same for both cultivars.

The percentage of the sum of linalool, nerol and geraniol concentrations (L+N+G) of wines to the sum of linalool, nerol and geraniol concentrations (L+N+G) of grapes, is also given in table VI. It is important that Muscat of Alexandria wines may contain at least 47 p. cent of the total monoterpenes of the grapes whereas Muscat lefko wines contain at least 36 p. cent. It is obvious that although the grapes of Muscat of Alexandria are not as rich in monoterpenes as Muscat lefko grapes are, the corresponding wines from Muscat of Alexandria preserve the greater part of the aromatic potential of the grapes or even exceed it (tables III and IV). Possibly, this variation is due to the different degree of ripeness of Muscat lefko and Muscat of Alexandria grapes. From the data of tables II and VI, it appears that Muscat of Alexandria wines that have a higher alcohol content (derived from grapes harvested at higher degree of ripeness) contain higher percentage of total monoterpenes compared to the wines of Muscat lefko.

TABLE VII
Influence of skin-contact maceration on monoterpene concentrations in wines (in µg/L)
Incidence de la macération pelliculaire sur la teneur en monoterpènes des vins (en µg/L)

		Control		Maceration		Control		Maceration	
		Vineyard 4 (1997)				Vineyard 1 (1998)			
	Compound	Free	Linked	Free	Linked	Free	Linked	Free	Linked
Muscat lefko	Linalool	286	43	366	100	419	255	586	315
	Nerol	42	480	48	726	46	853	73	1071
	Geraniol	48	429	84	666	82	624	101	804
	Citronellol	31	12	39	23	4	7	7	10
	α-Terpineol	163	5	172	7	47	13	65	23
		Vineyard 2 (1998)				Vineyard 7 (1998)			
	Linalool	200	172	265	252	285	210	611	742
	Nerol	33	654	89	788	52	672	152	758
	Geraniol	50	629	97	676	60	439	117	535
	Citronellol	6	5	8	6	7	10	17	10
	α-Terpineol	25	6	33	8	28	12	29	12
		Vineyard 2 (1997)				Vineyard 1 (1998)			
Muscat of Alexandria	Linalool	279	197	349	230	408	507	487	631
	Nerol	25	224	63	178	32	258	56	334
	Geraniol	83	722	301	681	96	682	179	872
	Citronellol	79	6	82	5	8	2	7	2
	α-Terpineol	70	4	100	4	14	7	26	10

©Vigne et Vin Publications Internationales (Bordeaux, France)

Another question arising from the above-mentioned results is why there is such a variation in the concentrations of monoterpenes among grapes and wines from the same cultivar. Probably this is related to the fact that terpene concentration in grape juices and wines depends on various factors such as vineyard conditions, grape maturation, grape storage, juice processing (pressing techniques, heat treatment, etc.) as well as wine-making parameters (yeasts and fermentation conditions) (MARAIS, 1983; DI STEFANO and CORINO, 1986; MACAULAY and MORRIS, 1993; GUNATA, 1994; REYNOLDS and WARDLE, 1997).

V - EFFECT OF MACERATION ON MONOTERPENE CONCENTRATIONS OF WINES

The effect of skin-contact treatment of the grape juice on monoterpene concentrations in Muscat wines for both years of experimentation is given in table VII. It is obvious that although individual monoterpenes behave differently, generally their concentrations are increased. Free and linked linalool is increased in wines derived from skin-contact treatment compared to the untreated ones in both cultivars. Free nerol concentration was in general doubled or even tripled in all treated wines. Also, linked nerol was higher in treated wines except one wine of Muscat of Alexandria in which the concentrations of linked nerol, geraniol and citronellol were decreased and linked α-terpineol remained stable. In all other wines, free and linked geraniol and α-terpineol were higher in treated wines than in the untreated ones. Free citronellol is generally increased in wines derived from skin-contact treatment although this increase is not so intense as it is for the other monoterpenes. Besides, in several wines linked citronellol remained almost unaffected by skin-contact.

Our results are in accordance with previous studies (MARAIS, 1987; REYNOLDS and WARDLE, 1997; MARAIS and RAPP, 1988) indicating that skin-contact for 4 and 15 h resulted in significant increases in the concentrations of several monoterpenes in Gewürztraminer wines. Furthermore, GÜNATA *et al.* (1985) reported the abundance of free terpenols, especially citronellol, nerol and geraniol in the skins of Muscat of Alexandria and nerol and geraniol in the skins of Muscat de Frontignan. However the studies of MARAIS and VAN WYK (1986) showed that skin-contact caused significant increases in monoterpene concentrations in a limited number of cases, namely linalool and α-terpineol in Weisser Riesling wines and nerol and geraniol in Bukettraube juices. It is also mentioned that linalool, nerol and geraniol mainly occur in the berry skin of Muscat and aroma related cultivars (BAYONOVE, 1992). Skin-contact would therefore cause additional quantities of these monoterpenes to be taken up in the juice. However the research of MACAULAY and MORRIS (1993) demonstrated that a 4 h skin-contact did not increase the potential volatile terpenes levels in Golden Muscat wines.

CONCLUSION

The aim of this work was to investigate the aromatic potential of two greek Muscat vine varieties, the relationships between free and glycosidically linked monoterpenes and their concentration in grapes and wines as well as the effect of skin-contact technique on monoterpene content as a mean to improve the vinification techniques and to adjust them to the quality of grapes in order to enhance the quality of the wines produced. The grapes of the cultivars Muscat lefko and Muscat of Alexandria from the Greek islands of Samos and Lemnos respectively are rich in monoterpene content. Muscat lefko grapes contain higher amounts of monoterpenes than those of Muscat of Alexandria. Several volatile alcohols are present in their free and glycoside form. The largest amount of linalool, nerol and geraniol found in grapes is linked with sugars. In wines, linalool is mainly found in its free form, whereas nerol and geraniol are mostly found in their linked forms. It is shown that when fermentation off skins is used, the resultant wines contain lower amounts of linalool, nerol and geraniol than the corresponding grapes. With respect to juice treatments, skin-contact for 8 h caused increases in monoterpene concentrations in both Muscat cultivars examined.

BIBLIOGRAPHICAL REFERENCES

BAYONOVE C., 1992. Les composés terpéniques. *In: Les acquisitions récentes en chromatographie du vin*. ed. by Lavoisier Tec & Doc, Paris, p. 99-119.

BELANCINC A., AGOSIN E., IBACACHE A., BORDEU E., BAUMES R., RAZUNGLES A. and BAYONOVE C., 1997. Influence of sun exposure on the aromatic composition of chilean Muscat grape cultivars Moscatel de Alejandria and Moscatel rosada. *Am. J. Enol. Vitic*., **47**, 2, 181-186.

BERTRAND A., GUEDES DE PINHO P. and ANOCIBAR-BELOQUI A., 1994. Les constituants majoritaires du vin. Les constituants volatils : teneurs trouvées, exemples d'analyses. *Feuillets verts OIV,* n° 971.

CORDONNIER R. and BAYONOVE C., 1981. Étude de la phase préfermentaire de la vinification : extraction et formation de certains composés de l'arôme ; cas des terpénols, des aldéhydes et des alcools en C6. *Connaissance Vigne Vin*, **15**, 269-286.

DI STEFANO R. and CORINO L, 1986. Caratteristiche chimiche ed aromatiche di vini secchi prodoti con

©Vigne et Vin Publications Internationales (Bordeaux, France)

Moscato bianco e giallo di Chambave e con Moscato bianco di canelli. *Riv. Vitic. Enol.*, **1**, 1-11.

DI STEFANO R., 1991. Proposition d'une méthode de préparation de l'échantillon pour la détermination des terpènes libres et glycosides des raisins et des vins. *Bull. OIV*, 219-223.

GÜNATA Y.Z., BAYONOVE C.L., BAUMES R.L. and CORDONNIER R.E., 1985. The aroma of grapes. Localisation and evolution of free and bound fractions of some grape aroma components cv. Muscat during first development and maturation. *J. Sci. Food Agric.*, **36**, 857-862.

GÜNATA Z., 1994. Étude et exploitation par voie enzymatique des précurseurs d'arômes du raisin de nature glycosidique. *Rev. Œnol.*, **74**, 22-27.

MACAULAY L.E. and MORRIS J.R., 1993. Influence of cluster exposure and winemaking processes on monoterpenes and wine olfactory evaluation of Golden Muscat. *Am. J. Enol. Vitic.*, **44**, 2, 198-204.

MARAIS J., 1983. Terpenes in the aroma of grapes and wines: A review. *S. Afr. J. Enol. Vitic.*, **4**, 2, 49-60.

MARAIS J., 1987. Terpene concentrations and wine quality of *Vitis vinifera* L. cv. Gewürztraminer as affected by grape maturity and cellar practices. *Vitis*, **26**, 231-245.

MARAIS J. and RAPP A., 1988. Effect of skin-contact time and temperature on juice and wine composition and wine quality. *S. Afr. J. Enol. Vitic.*, **9**, 1, 22-30.

MARAIS J. and VAN WYK C.J., 1986. Effect of grape maturity and juice treatments on terpene concentrations and wine quality of *Vitis vinifera* L. cv. Weisser Riesling and Bukettraube. *S. Afr. J. Enol. Vitic.*, 7, 1, 26-35.

OFFICE INTERNATIONAL DE LA VIGNE ET DU VIN. 1990. *Recueil des méthodes internationales d'analyse des vins et des moûts*. OIV, Paris.

OLIVEIRA J.M., MAIA O.M., BAUMES R.L. and BAYONOVE C. L., 1999. Teneur en norisoprénoïdes en C13 des cépages portugais Loureiro et Alvarinho. *In: XXIV Weltkongress für Rebe und Wein*, Mainz, Germany.

RAZUNGLES A., GUNATA Z., PINATEL S., BAUMES R. and BAYONOVE C., 1993. Étude quantitative de composés terpéniques, norisoprénoides et de leurs précurseurs dans diverses variétés de raisins. *Sci. Alim.*, **13**, 59-72.

REYNOLDS A.G. and WARDLE D.A., 1997. Flavour development in the vineyard: Impact of viticultural practices on grape monoterpenes and their relationship to wine sensory response. *S. Afr. J. Enol. Vitic*., **18**, 1, 3-18.

RIBÉREAU-GAYON P., BOIDRON J.N. and TERRIER A., 1975. Aroma of Muscat grape varieties. *J. Agric. Food Chem*., **23**, 1042-1047.

ROCHA S., COUTINHO P., COIMBRA M.A., DELGADILLO I. and DIAS CARDOSO, A. 1999. Study of the aromatic potentiality of two Bairrada white grape varieties: Maria Gomes and Bical. *In: XXIV Weltkongress für Rebe und Wein*, Mainz, Germany.

SALAHA M.J., LANARIDIS P., TSOUTSOURAS E., TZOUROU I. and KARAGIANNIS S., 1999. Arôme variétal de raisins et de vins issus des cépages Muscat blanc de l'île de Samos et Muscat d'Alexandrie de l'île de Lemnos. Effet de terroir et incidence de la macération pelliculaire. *In: V^e Symp. Int. Œnol.*, Bordeaux.

SEFTON M.A., FRANCIS I.L. and WILLIAMS P.J., 1993. The volatile composition of Chardonnay juices: A study by flavour precursor analysis. *Am. J. Enol Vitic.*, **44**, 4, 359-369.

WILSON B., STRAUSS C.R. and WILLIAMS P.J., 1984. Changes in free and glycosidically bound monoterpenes in developing Muscat grapes. *J. Agric. Food Chem.*, **32**, 919-924.

WILSON B., STRAUSS C.R. and WILLIAMS P.J., 1986. The distribution of free and glycosidically bound monoterpenes among skin, juice and pulp fractions of some white grape varieties. *Am. J. Enol. Vitic*., **37**, n°2, 107-111.

Reçu le 10 septembre 2001
accepté après révision le 28 février 2002

©Vigne et Vin Publications Internationales (Bordeaux, France)