Sensory properties and aroma compounds of sweet Fiano wine

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Abstract

The aroma of sweet Fiano wine, the most representative non-aromatic white wine variety in southern Italy, was evaluated by sensory and instrumental analysis to determine the influence of grape overripeness, drying and *Botrytis cinerea* infection. Sensory descriptive analysis was used to evaluate the sensory properties of wines. Gas chromatography/mass spectrometry (GC/MS), gas chromatography (GC) and gas chromatography/olfactometry (GC/O) techniques were used to identify and to determine the content of free and bound volatile compounds and their odour impact. A sensory descriptive analysis had revealed that the sensory descriptors such as citrus jam, dried apricot, dried figs, prune, honey and coconut, occur in sweet Fiano wine more than in base Fiano wine. Thirty five free volatile compounds had higher levels in sweet Fiano wine than in base Fiano wine, these components were mostly terpenes, β-damascenone, lactones, aldehydes and ketones. Moreover higher levels of terpenes, β-damascenone, benzyl alcohol and 2-phenylethanol were found in the bound volatile fraction of sweet Fiano wine. The main odour impact compounds in sweet Fiano wine were nerol, geraniol and linalool (orange flowers), vitispirane (camphor), lactones such as γ-nonalactone (coconut), δ-decalactone and γ-decalactone (apricot) and 1-octen-3-ol (mushroom). These differences appear to be due to the fact that grape overripeness and the drying process allows concentration of varietal aromatic compounds and an easier transfer of them from skins to must during vinification.
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Keywords: Volatile compounds; Sweet wine; Bound volatile compounds; Terpenes; C-13 norisoprenoids; GC/O

1. Introduction

In some grape growing areas in Europe, such as Germany, France, Hungary and Italy, the production of overripe grapes for special (sweet) wines has a long tradition. Riesling and Semillon grapes are the primary cultivars used in the production of these sweet wines from botrytized or non botrytized grapes. Other varieties, such as Furmint, Picolit, Gewurztraminer, Chenin blanc and Pinot blanc, are used depending on tradition and adaptation to local conditions. In Italy the main varieties used for this wine style are Malvasia and Moscato but also local varieties (Corvina, Rondinella and Molinara) are used as in the case of the famous Amarone wine.

A loss of firmness and a very soft texture, due to the senescence or aging of fruit tissues, are the most evident characteristics of overripe fruit. These physical features increase susceptibility to mechanical damage and infection by pathogens. When the grape is infected by *Botrytis cinerea* a number of important transformations occur, as well as the loss of water and the release of aroma compounds present in the skin (such as terpenes or C_{13}-norisoprenoids and monoterpenes precursors) into the must (Garcia, Chacon, Martinez, & Izquierdo, 2003; Marais, 1992; Park, Morrison, Adams, & Noble, 1991; Razungles, Babic, Bayonove, & Sapis, 1996).

Generally, the descriptive terms generated for sweet wines are floral, thyme flower, tropical fruit, passion fruit, mango, citrus, orange peel, apricot, dried apricot, peach, marmalade, honey and caramel (Croser, 1989). For Zinfandel the main influence of grape overripeness on wines appears to be intensified ethanol aromas, bitterness, viscosity, and black pepper and berry flavours (Noble & Shannon, 1987).

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The volatile compounds identified in sweet wine belong to different chemical classes (Maarse, Visscher, Willemsens, & Boelens, 1992). In particular, a recent study on Tokaj Aszù wine shows that hydroxy-, oxo-, and dicarboxylic acid esters, responsible for coconut, chocolate, peach and fruity odour notes, were present in much higher levels than base wines (Miklósy, Kalmár, Pölös, & Kerényi, 2000; Miklósy & Kerényi, 2004).

Recently, interest in sweet wines has increased enormously and various other grape varieties, traditionally destined for dry white wine production, have been employed for these wines.

The aim of this study was to determine the influence of overripeness, drying and *Botrytis cinerea* on the volatile composition and quality of white wine. The experiment was conducted on the "Fiano" cultivar, the most representative white wine variety in the Campania region of Italy. The sweet and base Fiano wines were analyzed by sensory descriptive analysis and by means of gas-chromatography, gas-chromatography/mass spectrometry and gas-chromatography/olfactrometry.

2. Materials and methods

2.1. The experimental wines

Fiano grapes were hand-harvested at full maturation (22 °Brix) in vineyards located in the town of Taurasi (AV), a DOCG area in the Campania region. For Fiano base wine, 2000 kg of grapes were crushed (0.9 atm) and SO_2 (50 mg/l) and pectic enzyme (1 g/hl) were added. Must was immediately cooled to 12 °C and was submitted to static decantation (80–100 NTU). Inoculations were carried out at 30 g/hl, after yeast (R7 Lalvin, Lallemand Inc., Castel d'Azzano – Italy) rehydration in warm water for 30 min, as described by the manufacturer. Fermentation took place in six *barriques* (*Troncay*) at 12 °C. Upon completion of alcoholic fermentation, wines were cold stabilized for a 3 month period at 10 °C, racked with 30 mg/l of SO_2, and after 20 days bottled. For the production of sweet Fiano wine the grapes were harvested in an advanced state of maturation (26 °Brix) with a percentage of *Botrytis cinerea* at 20% and were dried on racks until a concentration of 32 °Brix of sugars. The vinification procedure used was similar to that employed for base Fiano wine with the exception that from 2000 kg of grapes only three *barriques* were filled with must and that before bottling 100 mg/l of SO_2 were added.

2.2. Sensory descriptive analysis

The panel of judges consisted of eight oenology students attending the Faculty of Agriculture at Foggia University. They had been selected from a group of 20 people on the basis of their sensorial performance. A sensory descriptive analysis was performed in according to Moio, Schlich, Issanchou, Etievant, and Feuillat (1993). All the judges had extensive experience in wine tasting, and some of them already took part in descriptive analysis studies. The wines were subjected to sensory descriptive analysis at 12 °C in three different sittings.

A descriptive analysis of the odour was performed using the technique of free vocabulary. During the descriptive analysis of the wine odour, the judges were asked to use not more than five descriptors and to not use hedonistic terms such as pleasant, fine, agreeable, fragrant, elegant, complex, fresh, flat, thin; or else gustative terms such as sweet, bitter, salty, metallic; or else those related to technological inconveniences such as reduced, oxidized, lees, maderized wine.

Correspondence analysis (CA) was carried out to evaluate sensory data. Statistical data processing was performed using the Statgraphics plus (5-PC) statistical pocket (Manugistics Inc., 1999).

2.3. Extraction and analysis of free and bound volatile compounds

For high resolution gas chromatographic (HRGC) analysis of free volatile compounds, 200 ml of wine obtained after the whole contents of three equal bottles had been mixed, was submitted to continuous liquid–liquid extraction for 1.5 h with 20 ml of freon 113. One millilitre of an alcoholic solution of 2-methyl-1-pentanol (200 mg/l) was added as internal standard. The organic phase was recovered in a separating funnel, dried over Na_2SO_4, and concentrated (~40 times) first in a Kuderna-Danish concentrator (Supelco, Bellefonte, PA) and than under a stream of pure N_2 (1.5 l/min) for GC and GC–MS analysis.

C-18 reverse-phase solid phase extraction (SPE) was adopted for the extraction of bound aroma compounds from wines, as previously reported by several authors (Mateo, Gentilini, Huerta, Jiménez, & Di Stefano, 1997; Moio, Ugliano, Gambuti, Genovese, & Piombino, 2004; Ugliano, Genovese, & Moio, 2003). Twenty-five milliliters of sample was diluted 1:1 with water, filtered at 0.45 μm, loaded on a previously activated 1 g C-18 cartridges (Phenomenex, Torrance, CA), and eluted at ~3 ml/min. The cartridge was then washed with water, followed by dichloromethane for removal the free volatiles compounds and methanol for the recovery of the glycoconjugated fraction (bound volatiles). The methanol fraction was concentrated to dryness and redissolved in 3 ml of phosphate-citrate buffer at pH 5.0 containing 30 mg of Rohapect C β-glucosidase enzyme (Rohm, Darmstadt, Germany). After 16 h of incubation at 40 °C, 125 μl of an alcoholic solution of 2-octanol was added as internal standard, and the mixture containing free aglycons was loaded on a C-18 SPE cartridge, and the volatiles were extracted with 5 ml of dichloromethane. The extract, was dried over Na_2SO_4, and concentrated (~40 times) first in a Kuderna-Danish concentrator (Supelco, Bellefonte, PA) and than under a stream of pure N_2 (1.5 l/min) for GC and GC–MS analysis. Each extraction was carried out in triplicate.

A 1 μl aliquot of each concentrated extract was injected in splitless mode into a Hewlett–Packard 5890 chromato-

graph equipped with a split/splitless injector (Hewlett–Packard, Avondale, PA), a J&W DB-Wax column (30 m length, 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA), and a flame ionization detector (FID). The temperature program used was 40 °C for 3 min, raised at 2 °C/min to 220 °C, and held for 15 min at maximum temperature. Carrier gas (He) velocity was 37 cm/s. Both detector and injector temperatures were maintained at 250 °C.

Identification of compounds was performed by comparison of their retention time with those of pure reference standards. Comparison of mass spectra stored in the NIST database with those obtained for each compound on an HP 5972 quadrupole mass spectrometer coupled with an HP5890 gas chromatograph was also carried out. The same column and the same temperature program of HRGC were employed during this analysis. Electron impact mass spectra were recorded with an ion source energy of 70 eV. The injector port and the ion source were maintained at 250 and 230 °C, respectively.

2.4. Gas chromatography–olfactometry analysis

GC–O analysis was performed on extracted free volatile compounds using a 5890 Hewlett–Packard gas-chromatograph equipped with a same column of HRGC analysis connected with an Hewlett–Packard "Y splitter deactivated", allowing the effluent to be split between the sniffing port and flame ionization detector (FID). Dilutions of Aroma Extract Dilution Analysis (AEDA) were done sequentially by volume (1:3). A 1.5 μl splitless injection of extract was made. Gas chromatographic conditions were the same as those described for HRGC analysis. Two experienced judges working independently did the sniffing.

3. Results and discussion

3.1. Sensory descriptive analysis

In Fig. 1, a biplot of the correspondence analysis (CA) is reported. The sensorial attributes of experimental base
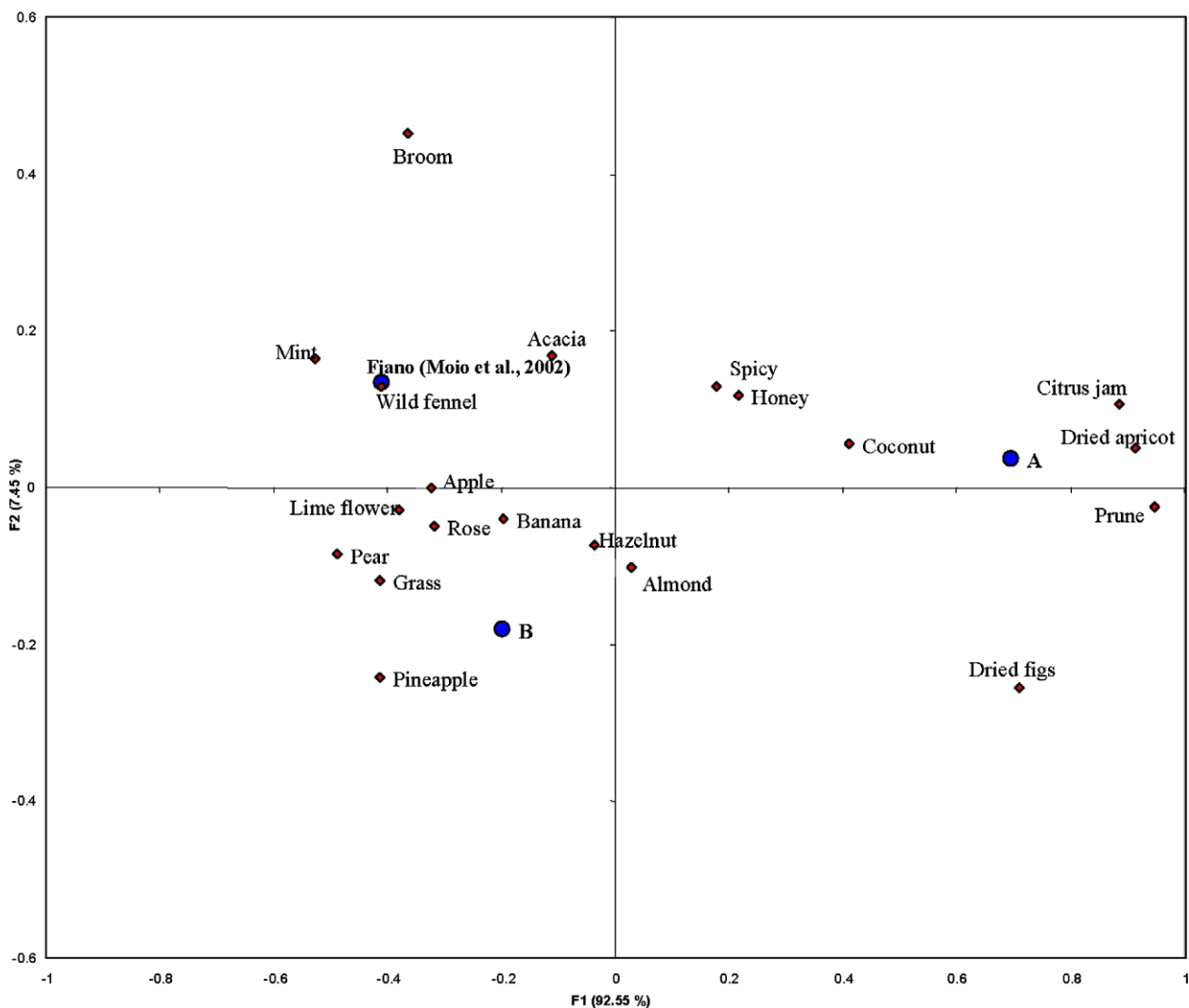

Fig. 1. Correspondence analysis (CA) of sensorial attributes of sweet Fiano wine (A), base Fiano wine (B) and Fiano wine analyzed and reported in a previously paper (Moio et al., 2002).

Fiano wine (B) is very similar to that obtained with a typical Fiano wine reported in a previous study (Moio et al., 2002). They were characterized mainly by fruity notes (banana, apple, pear and pineapple), flower notes (lime, rose and acacia) and vegetable notes (mint, grass and wild fennel). On the contrary, in the sweet Fiano wine (A) these descriptors were less important, while the descriptors citrus jam, dried apricot, dried figs, prune, honey and coconut increase. Descriptive terms used for sweet Fiano wines (A) are very similar to those reported for botrytized wines

Table 1
Quantitative data of volatile compounds identified in the sweet Fiano wine (A) and base Fiano wine (B)

Compound	Concentration (µg/l)[a]				Compound	Concentration (µg/l)[a]			
	A		B			A		B	
Esters					*Terpenes*				
Ethyl 2-methylpropanoate	156	±14	776	±181	p-Cimene	8.1	±0.5	nf	
2-Methylpropyl acetate	1759	±185	1959	±1110	cis-Linalool oxide	70.4	±3.6	49.1	±1.9
Ethyl butanoate	375	±17	925	±14	trans-Linalool oxide	31.3	±1.4	14.6	±0.6
Ethyl 2-methylbutanoate	61.1	±4.1	184	±1.8	Linalool	120	±5.0	11.8	±0.6
Ethyl 3-methylbutanoate	107	±5	340	±10	Terpinen-4-ol	190	±7	8.0	±1.6
3-Methylbutyl acetate	768	±28	938	±20	α-Terpineol	196	±8	129	±6
Ethyl hexanoate	1147	±30	3781	±116	Nerol	nd		nd	
Hexyl acetate	<3.7		24.7	±1.4	Geraniol	22.4	±0.4	<3.7	
Ethyl heptanoate	17.6	±0.6	<3.7						
Ethyl lactate	287	±23	1283	±75	*Lactones*				
Ethyl 2-hydroxy-3-methylbutanoate	8.8	±0.8	24.3	±1.1	γ-Butyrolactone	219	±22	209	±13
Ethyl octanoate	1246	±38	6152	±284	Valerolactone	76.0	±3.1	nf	
Ethyl 2-hydroxycaprinoate	94.9	±9.8	276	±6	cis-Wisky lactone	165	±7	nf	
Diethyl propandioate	36.8	±3.4	36.5	±2.4	trans-Wisky lactone	274	±9	20.3	±3.1
4-Oxoethyl-pentanoate	45.4	±4.3	nf		γ-Nonalactone	43.2	±6.1	6.3	±0.3
Ethyl 2-furoate	40.9	±2.6	104	±4	γ-Decalactone	15.5	±0.9	3.7	±0.1
Ethyl decanoate	95.6	±3.1	1529	±214	δ-Decalactone	22	±1	4.0	±0.1
Isoamyl octanoate	<3.7		52.2	±5.2					
Diethyl succinate	13,011	±589	22673	±1179	*Aldehydes and ketones*				
Ethylphenyl acetate	181	±6.7	166	±8	Diacetyl	nd		nd	
2-Phenylethyl acetate	144	±7	308	±12	Acetoin	<3.7		<3.7	
Ethyl 3-hydroxyhexanoate	15.5	±2.0	nf		Furfural	1260	±65	<3.7	
Diethyl malate	1134	±79	2908	±114	Benzaldehyde	204	±41	9.9	±0.6
Ethyl cinnamate	27.3	±1.2	10.4	±1.2	5-Methylfurfural	30.6	±3.7	24.4	±0.9
Ethyl vanillate	138	±18.1	nf		Acetophenone	nd		nf	
					Furaneol	nd		nd	
Alcohols					Homofuraneol	nd		nd	
2-Methyl-1-propanol	118	±15	202	±29	3,4-Dihydro-8-hydroxy-3-methyl-	31.2	±6.9	nf	
1-Butanol	<3.7		7.8	±2.0	1-H-2-benzopyran-1-one				
3+2-Methyl-1-butanol	16,800	±1197	33663	±2401					
4-Methyl-1-pentanol	11.3	±1.5	<3.7		*C13-norisoprenoid*				
1-Hexanol	805	±41	1249	3030	Vitispirane	nd		nf	
3-Hexen-1-ol (E)	35.8	±3.4	69.4	±2.1	TDN	7.8	±1.3	9.1	±0.8
1-Octen-3-ol	213	±8	<3.7		β-Damascenone	10.4	±0.8	<3.7	
1-Heptanol	27.9	±1.8	nf						
2-Ethylhexanol	18.6	±2.0	nf		*Phenols*				
2-Phenylethanol	7335	±456	19328	±502	Guaiacol	<3.7		<3.7	
					Eugenol	41.1	±2.5	11.2	±1.0
Acids					4-Vinylguaiacol	265	±12	80.9	±3.7
Acetic acid	122	±37	141	±27	Syringol	75	±3.1	20.0	±1.5
2-Methylpropanoic acid	285	±7	225	±21	Isoeugenol	nd		nd	
Butanoic acid	93.0	±6.2	154	±15					
3-Methylbutanoic acid	342	±28	513	±25	*Other*				
Hexanoic acid	1024	±133	4381	±103	3-Methylthio-1-propanol	10.5	±2	17.6	±4
Heptanoic acid	14.8	±2.7	nf		N-3-methylbutyl acetamide	59.6	±4.4	nf	
2-Hexanoic acid	31.2	±3.0	125	±8					
Octanoic acid	3010	±411	19451	±478					
Nonanoic acid	<3.7		nf						
Decanoic acid	484	±87	5655	±225					
Benzoic acid	87.6	±10.1	<3.7						
Phenyl acetic acid	nd		nd						

nf, not found; nd, not determined since the relative peak contained more than one component as confirmed by mass-spectrometry.
[a] Means of triplicate analysis.

obtained from different grape varieties (Croser, 1989). The descriptors hazelnut and almond, already frequently used in the oenological literature to describe Fiano aroma, did not show significant differences.

3.2. Free volatile compounds analysis

A total of 81 compounds were identified in the volatile fraction of the Fiano wines: 25 esters, 10 alcohols, 12 acids, 8 terpenes, 7 lactones, 6 ketones, 5 phenol, 3 aldehydes, 3 C-13 norisoprenoid, 1 sulfur compound and 1 nitrogen compound. The identified volatile compounds, grouped into chemical class with the concentration, are given in Table 1. Eight volatile compounds could not be determined since they were present in trace levels and the relative peak contained more than one component as confirmed by mass-spectrometry. They are: diacetyl, nerol, vitispirane, acetophenone, furaneol, homofuraneol, isoeugenol and phenyl acetic acid. Results reported in Table 1 indicate that only 35 volatile compounds were present at a higher level in sweet Fiano wine (A) than in base Fiano wine (B). These components belong to the terpenes, C-13 norisoprenoids (β-damascenone), lactones and aldehydes.

Terpenes are responsible for floral aromas of Muscat and Gewürztraminer wines, honey notes of Tokay (Pisarnitskii, 2001) and aroma of aged Muscat wines (Rapp, Mandery, & Niebergall, 1986). Generally their concentration in grape gradually rises during ripening until around maturity, after which concentrations fall off (Gunata, Bayonove, Baumes, & Cordonnier, 1985; Wilson, Strass, & Williams, 1984). Since around 50% of the total monoterpenes were found in the grape skin (Park et al., 1991), the high level of terpenes detected in sweet Fiano wine could be derived from the structural degeneration of it. The higher content of α-terpineol and linalool oxides in sweet wine may be correlated to a higher level of linalool in overripe grape because these compounds originate, respectively, from cyclization and oxidation of linalool (Rapp & Marais, 1993). However these products can originate also from the metabolic activity of *Botrytis cinerea* (Bock, Benda, & Schreier, 1986).

Norisoprenoids are volatile compounds that could come from the direct degradation of carotenoid molecules such as β-carotene, lutein, neoxanthin and violaxanthin (Kanasawud & Crouzet, 1990; Marais, 1992; Schreier, Drawert, & Bhiwapurkar, 1979). Carotenoids are unstable compounds, whose degradation can occur in presence of oxygen, elevated temperatures and exposure to the sun (Rapp & Marais, 1993). Subsequently both in the grape and in the wine, odour compounds are formed which have an important role on the varietal character of wines because they have a very low odour threshold. Examples of norisoprenoid odorants are α- and β-ionone (threshold 2.6 and 0.09 ppb; Ferreira, Lopez, & Aznar, 2002), β-damascenone (threshold 0.05 ppb in wine; Ferreira et al., 2002), vitispirane and 1,1,6-trimethyl-1,2-dihydronaphtalene (TDN) (threshold 20 ppb in wine; Simpson, 1978).

These last two compounds, absent in new wine, are formed in wine during ageing and are present in relatively large amounts in aroma volatiles of matured wines (Ferreira & Guedes de Pinho, 2004; Rapp & Marais, 1993). However the levels of TDN and vitispirane, respectively, kerosene-like and camphor odours, found in the sweet Fiano wine do not seem to be determinant for the aroma. Among C_{13}-norisoprenoids, β-damascenone is one of the most important compounds found at higher level in sweet Fiano wine than in base Fiano wine (three times) and it exhibits a complex smell of exotic flowers, stewed apple and tea (Cunningham, Acree, Barnard, Butts, & Braell, 1986; Moio et al., 2002; Ohloff, 1978; Renold, Naf-Muller, Keller, Willhalm, & Ohloff, 1974). The higher level detected in sweet wine may be due not only to major concentration in overripe and dried grape but also to higher contents of its glycosidic precursors (Wilson et al., 1984). In fact it is well known that their level could increase in wine by hydrolysis and rearrangement of norisoprenoid glycoside during the wine-making process (Gunata et al., 1985). Its increase could also be due to oxygen and SO_2 effect (Ferreira & Guedes de Pinho, 2004).

Six γ-lactones and one δ-lactone were identified with predominance of C4 and *cis* and *trans* whisky lactones. All of them were present in higher levels in sweet Fiano wine than base Fiano wines particularly γ-valerolactone (dihydro-5-methyl-2(3H)-furanone) and whisky lactones. γ-Butyrolactone, present in every fermented product, probably arises from glutamic acid or related compounds (Muller, Kepner, & Webb, 1973). On the contrary the presence

Table 2
Quantitative data of main bound aroma compounds in the sweet Fiano wine (A) and base Fiano wine (B)

Compounds	Concentration (µg/L)[a]			
	A		B	
3-Methyl-1-butanol	160	±12	38	±1
2-Octanone	92	±6	11	±0.3
1-Hexanol	116	±9	18	±0.8
(Z)-3-hexen-1-ol	10	±1	3	±0.2
(E)-3-hexen-1-ol	1	±0.1	2	±0.1
cis-Linalool oxide	17	±3	3	±0.2
1-Octen-3-ol	11	±2	4	±0.1
trans-Linalool oxide	3	±0.2	2	±0.1
Benzaldehyde	5	±0.1	4	±0.2
Linalool	50	±3	2	±0.1
1-Octanol	12	±1	5	±0.2
α-Terpineol	19	±1	5	±0.1
Epoxylinalool	25	±2	6	±0.2
Nerol	29	±2	13	±0.4
β-Damascenone	5	±0.2	1	±0.1
Hexanoic acid	8	±0.3	2	±0.1
Geraniol	34	±1	9	±0.3
Esohydroxycineol	17	±1	3	±0.3
Benzyl alcohol	193	±13	51	±3
2-Phenylethanol	167	±10	61	±3
3-Phenylpropanol	13	±0.5	1	±0.1
Octanoic acid	136	±8	31	±1

[a] Means of triplicate analysis.

Table 3
Odour-active compounds detected in sweet and base Fiano wines

Retention time (min)	Odour	Identification	Compounds
5.27	Apple	RS	Ethyl acetate
5.47	Butter	RS	Diacetyl
6.98	Kiwi	EI, RS	Ethyl butanoate
7.47	Red fruits	EI, RS	Ethyl 2-methylbutanoate
7.95	Exotic fruits	EI, RS	Ethyl 3-methylbutanoate
9.63	Banana	EI, RS	3-Methylbutyl acetate
10.30	Grass	EI, RS	1-Butanol
12.77	Grass	EI, RS	3-Methyl-1-butanol
13.60	Apple	EI, RS	Ethyl hexanoate
16.19	Toasted nuts	NI	
19.80	Grass	EI, RS	Z-3-hexen-1-ol
20.35	Orange flowers	NI	
20.69	Pineapple	EI, RS	Ethyl octanoate
20.83	Vinegar	EI, RS	Acetic acid
21.47	Mushroom	EI, RS	1-Octen-3-ol
22.46	Mushroom	NI	
23.34	Camphor	EI	Vitispirane
24.24	Flowers	NI	
24.60	Orange flowers	EI, RS	Linalool
25.10	Cheese	EI, RS	2-Methylpropanoic acid
27.08	Cheese	EI, RS	Butanoic acid
27.64	Flower	EI, RS	Ethyl decanoate
27.75	Acacia honey	EI	Acetophenone
28.32	Cheese	EI, RS	3-Methylbutanoic acid
29.30	Potato, garlic	EI, RS	3-Methylthio-1-propanol
30.00	Cheese	EI, RS	Pentanoic acid
30.80	Truffle, kerosene	EI	TDN
32.99	Orange flowers	EI, RS	Nerol
33.10	Rose	EI, RS	2-Phenylethyl acetate
33.30	Tea, flower	EI, RS	β-Damascenone
33.70	Cheese	EI, RS	Hexanoic acid
34.06	Orange flowers	EI, RS	Geraniol
34.20	Smoky	RS	Guaiacol
35.16	Strawberry	EI	Ethyl 3-hydroxyhexanoate
35.67	Coconut	EI, RS	E-wisky lactone
35.80	Rose	EI, RS	2-Phenylethanol
37.48	Coconut	EI, RS	γ-Nonalactone
38.50	Cheese	EI, RS	Octanoic acid
39.45	Strawberry	RS	Furaneol
39.60	Apricot	NI	
40.45	Caramel	EI	Homofuraneol
41.30	Apricot	EI, RS	γ-Decalactone
41.50	Clove	EI, RS	Eugenol
42.20	Plum, dried figs, dried apricot	NI	
42.40	Citrus jam	NI	
43.40	Apricot	EI, RS	δ-Decalactone
44.10	Smoky	EI, RS	Syringol
44.66	Licorice, wood, coffee	NI	
45.64	Spice	NI	
45.90	Almond	NI	
46.83	Clove	EI, RS	Isoeugenol

Table 3 (continued)

Retention time (min.)	Odour	Identification	Compounds
47.24	Pepper		NI
47.40	Medicinal		NI
49.86	Medicinal		NI
53.70	Wood, spice		NI
55.35	Spice		NI
57.69	Honey	EI, RS	Phenyl acetic acid

NI, not identified; EI, electron impact mass spectrometry; RS, identification was based on agreement with the reference substance.

of whisky lactones derives exclusively from the use of the *barriques* (Moio, Del Prete, Diana, & Valentino, 1999). The high level of whisky lactones detected in sweet Fiano wine, together with other "wood compounds" such as eugenol, syringol and isoeugenol (Table 1), is due to the high alcoholic level of the sweet wine that facilitates the extraction of these compounds from the wood (Maga, 1989). On the other hand lactones seem to be the key aroma of the Tokaji wines (Miklósy et al., 2000; Miklósy & Kerényi, 2004), probably for the metabolic action of *Botrytis cinerea*.

Among aldehydes, furfural and benzaldehyde show a high increase in sweet Fiano wine, respectively, 340.5 and 20.6 times. Furfural is formed by the degradation of hemicellulose during toasting of the barrel (Chatonnet, Boidron, & Pons, 1989). However, it may be assumed that the furfural present in aged wines does originate also from the carbohydrates occurring in wines during the ageing period (Rapp & Mandery, 1986). Furfural is characterized by a toasted almond odour and is probably not important to the aroma of sweet wine because its level is low with respect to its odour threshold (14.1 mg/l; Ferreira et al., 2002). Benzaldehyde has a bitter almond odour. It is one of the compounds typically associated with *Botrytis cinerea* infection (Goetghebeur, Nicolas, Brun, & Galzy, 1992). Benzaldehyde in wine is probably formed by the oxidation of the benzyl alcohol or by action of the microorganisms on the aromatic aminoacids (phenylalanine) or on the phenol compounds of the grape or on some secondary compounds such as phenyl acetic acid and *p*-hydroxybenzoic acid (Cook, 1958; Delfini et al., 1991; Gomez-Cordoves & Khayyat, 1982; Wildenradt & Singleton, 1974). Since phenyl acetic acid has already been identified as the main odorant in Fiano wine (Moio et al., 2002), it is reasonable to hypothesize that benzaldehyde could derive from it.

The major fermentation compounds such as alcohols, ethyl esters, acetates and fatty acids were detected at higher levels in base Fiano wine than sweet Fiano wine. This is exclusively due to the metabolic activity of the yeasts. In fact, yeast is able to synthesize all amino acids that it requires from ramified amino acids by the Ehrlich pathway. In this case yeast produces refuse products such as fusel alcohols. This phenomenon is enhanced when the

medium is poor in glutamic acid and ammonia. Since the must, from overripe grape, contains a high free amino acid level, particularly glutamic acids (Kliewer, 1968), yeast produces low levels of fusel alcohols and other volatile by-products. The decrease of ethyl esters and acetates are probably due also to the metabolic activity of *Botrytis cine-*

rea (Ribéreau-Gayon, Dobourdieu, Donèche, & Lonvaud, 2003, chap. 13). 1-Octen-3-ol, responsible for the mushroom odour (Serot, Prost, Visan, & Burcea, 2001), shows a high level in sweet Fiano wine (57.6 times). This is a typical by-product of the metabolic activity of *Botrytis cinerea* (Yunome, Zenibayashi, & Date, 1981).
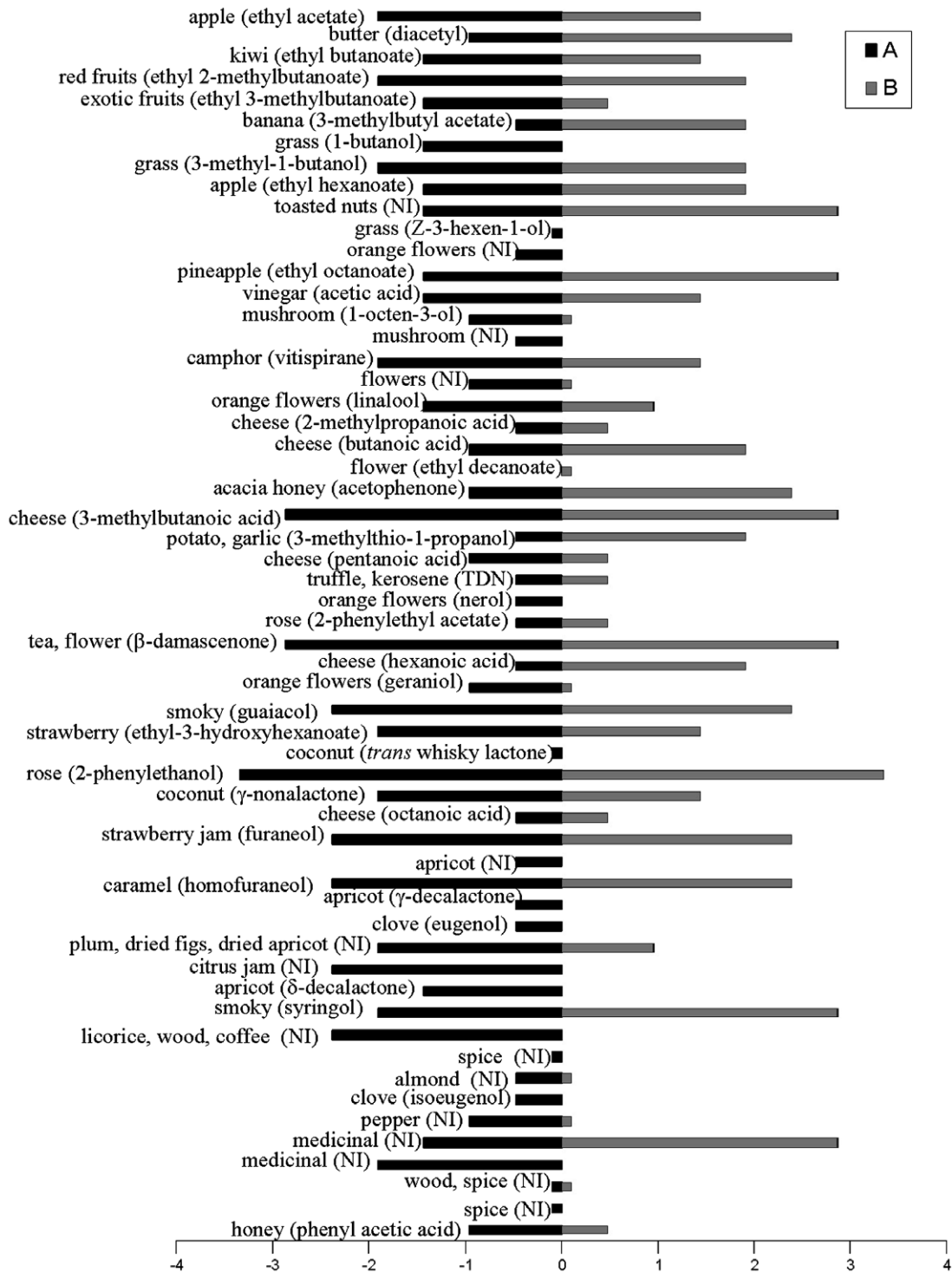
Fig. 2. Aromagrams of the sweet Fiano wine (A) and base Fiano wine (B).

3.3. Bound volatile compounds analysis

It has been established that bound volatile compounds are flavourless precursor compounds of grapes which could be transformed during processing into flavour active compounds. Particularly ninety percent of total terpenes occurred as glycosides in wine (Park et al., 1991), indicating their potential contribution to wine aroma. In Table 2 the level of bound aroma compounds detected in the volatile fraction of sweet Fiano wine (A) and base Fiano wine (B) are reported. Sweet Fiano wine exhibited the highest levels of terpenes, β-damascenone, benzyl alcohol and 2-phenylethanol to base Fiano wine. β-Damascenone, together with linalool, are the principal odour compounds released during aging of wine from the glycosydic form (Sefton, Francis, & Williams, 1993; Winterhalter, Sefton, & Williams, 1990), nevertheless modest levels have been found in sweet wine. Since β-damascenone formation involves other precursory glycosides as well as glycosilated 3-hydroxydamascenone, it is possible that during aging its contribution to wine aroma increases. Similarly TDN, absent in glycosidic form in Fiano wines, is released during wine aging by different transformations after the liberation of the 2,6,10,10-tetramethyl-1-oxoaspiro-[4,5]-dec-6-en-2,8-diol as the glycosydic precursor (Winterhalter, 1991). Finally it is interesting to note the higher level of bound benzyl alcohol in sweet Fiano wine because it could be the source of benzaldehyde by means of wine oxidation (Delfini et al., 1991).

3.4. GC–olfactometry analysis

Gas chromatography–olfactometry analysis revealed 57 odorous compounds in sweet and base Fiano wine but only 42 of them were identified (Table 3). A comparison between AEDA profiles of sweet Fiano wine (A) and base Fiano wine (B) is shown in Fig. 2. Nineteen odour compounds of the 81 volatiles identified in sweet Fiano wine (A) differed significantly from base Fiano wine (B). The main compounds were ethyl 3-methylbutanoate (exotic fruits), 1-butanol (grass), 1-octen3-ol (mushrooms), vitispirane (camphor), linalool, nerol and geraniol (orange flowers), γ-nonalactone (coconut), γ and δ-decalactone (apricot), eugenol and isoeugenol (clove) and phenyl acetic acid (honey). Eleven odour peaks of sweet Fiano wine, were not identified. They showed floral, apricot, plum, citrus jam, licorice, almond, pepper and medicinal odour notes. Base Fiano wine (B) exhibited other aroma compounds as well as ethyl esters, fatty acid, diacetyl, acetophenone, 3-methylthio-1-propanol and syringol, characterized, respectively, by fruit, cheese, butter, acacia honey, potato and smoky odours. The olfactometric analysis revealed that 15 aroma compounds showed a similar AEDA value in both wines even if, in some cases, they had different concentrations in the two Fiano wines. This is probably due to the limit of the olfactometry technique. Among them there was 2-phenylethanol (rose), 3-methyl-1-butanol (grass), ethyl 2-methylbutanoate (red

fruits), 3-methylbutanoic acid (cheese) and β-damascenone (tea).

In conclusion, the main influences of grape overripeness and drying on wines appear to be the enhancement of dried fruits (apricot, plum, figs), honey, citrus jam and coconut aromas. Moreover a strong effect on free and bound volatile composition was detected. The level of several volatile compounds is higher in sweet wine. These components belong to the terpenes, C-13 norisoprenoids, lactones and aldehydes. On the basis of experimental data obtained, it was possible to assign a role of primary importance to the skin of grape vine berries as a source of varietal aromatic compounds when the grape is submitted to overripening and the drying process as confirmed by the complexity of the aromagram detected. Nevertheless ulterior analyses, to identify other important aroma compounds of sweet wine, are necessary.

Acknowledgement

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