DETERMINATION OF VOLATILE COMPOUNDS IN SULTANIYE WINE BY SOLID-PHASE MICROEXTRACTION TECHNIQUES

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Volatile compounds of wines made from Sultaniye grape varieties grown in Denizli-Turkey were investigated. Volatile compounds in wines were extracted by headspace and immersion solid-phase microextraction (SPME) methods and identified by GC-MS. According to the results of analyses, esters were mainly responsible for the flavor of Sultaniye wine, and among these, ethyl decanoate, ethyl octanoate, ethyl hexanoate, and 3-methylbutyl acetate were found to be dominant.

Key words: Sultaniye wine, SPME, volatiles, ester.

Aroma is one of the most important attributed quality character in wines. Aroma, which is constituted of various substances, plays a role in sensorial properties. In the previous studies more than 1000 aroma compounds were identified in wines [1–3].

The aroma of wine depends on many varietal or fermentative compounds, which are present in highly variable amounts and are mainly esters, alcohols, terpenes, lactones, acids, and sulfur compounds [1, 5]. Among these, esters are of crucial importance as they provide pleasant aroma sensations in wines. In fresh and young wines the aroma changes according to the composition of ester compounds, which gives the typical fruity flavor. The volatile compounds, especially esters, which are found in small amounts in wines are produced through metabolic pathways during the fermentation. Esters which give a fruity odor to wines are produced via an enzymatic pathway during the alcoholic fermentation, especially if wines are produced from neutral varieties [1, 4, 5].

In the grape and wine, the amount of aroma compounds changes from nanogram to milligram. The identification of aroma compounds is very difficult because they are found in trace amounts in wines. For this reason, aroma analysis should be done using very sensitive, versatile, and reliable techniques. In aroma analysis, the most important step is the separation of aroma compounds from grape juice and wine. Extraction of these compounds can be difficult if inappropriate methods are used. Different extraction methods such as liquid-liquid extraction, Amberlite XAD-2, inert gases, C-18 resin, and solid phase microextraction (SPME) techniques have been developed for this reason [6, 7].

The SPME technique has been an inexpensive, rapid, and versatile method for the extraction of volatile compounds in the last decade [8, 9]. In the SPME technique, both headspace (HS) and immersion (Im) methods can be used in the extraction of aroma compounds directly using suitable fibres [10].

The aim of this study was the detection of volatile compounds in Sultaniye wines using HS-SPME and Im-SPME techniques.

The aroma compounds of Sultaniye wine characterized by GC/MS analysis are given in Table 1. A total of 16 volatile aroma compounds were identified in the wines, including esters (11), acids (3), alcohol (1), and lactone (1). Esters were found to be the most abundant aroma compounds in the wine samples. Volatile esters of the wines can originate from raw material and compounds biosynthesized during alcoholic fermentation by the yeast. They are among the key compounds in the fruity flavors of young wines. Esters are also considered for their fruity and pleasant aroma [4, 5].

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TABLE 1. Aroma Compounds Identified in Sultaniye Wine by GC/MS

RT	Compounds	HS-SPME, %	IM-SPME, %	Odor
4.84	3-Methylbutyl acetate	4.3	9.2	Banana [17]
7.54	Ethyl hexanoate	2.7	5.8	Strawberry, green apple, banana [17, 18]
7.92	Hexyl acetate	1.7	3.7	Banana, pear [19]
10.41	Phenyl ethyl alcohol	Tr.	Tr.	-
12.66	Octanoic acid	0.7	3.3	-
13.27	Ethyl octanoate	32.9	44.4	Ananas, pear [18]
14.58	Phenyl ethyl acetate	Tr.	Tr.	Flowery, rose, honey [17]
18.48	Decanoic acid	0.4	7.5	-
18.68	Ethyl-9-decenoate	2.3	1.9	-
19.04	Ethyl decanoate	43.5	21.7	Fruity, grape [118]
20.28	γ-Decalactone	-	Tr.	Peach [17, 18]
20.41	Isoamyl octanoate	0.4	Tr.	Flowery, fruity [17]
23.49	Dodecanoic acid	-	Tr.	-
24.37	Ethyl dodecanoate	7.9	1.6	-
25.66	Isoamyl decanoate	0.7	Tr.	-
33.77	Ethyl hexadecanoate	Tr.	Tr.	-

RT: retention time. Tr.: trace.

Our results were similar to those of previous studies [10–13]. Among the esters ethyl octanoate and ethyl decanoate were found to be the most abundant ones. They were followed by 3-methyl butyl acetate and ethyl hexanoate. Analytical results and odor characteristics of the compounds characterized are given in Table 1. In the sensory evaluation, especially ananas, green apple, and banana odors were characterized in Sultaniye wines [14].

The three fatty acids identified in the wine were octanoic, decanoic, and dodecanoic acids. Fatty acids in wines are derived from yeast during fermentation, and from the firm tissues of the grapes [5, 15]. As can be seen in Table 1, the Im-SPME technique showed a higher sensitivity than the HS-SPME technique for the detection of fatty acids from the wine.

In Sultaniye wines, trace amounts of phenyl ethyl alcohol and γ-decalactone were also determined. γ-Decalactone was only found in the Im-SPME technique (Table 1). This compound has a pleasant aroma, with peach attribute [16].

In conclusion, this study on volatile compounds of Sultaniye wine showed that this wine was characterized by the presence of high levels of ester compounds, and both extraction techniques were suitable for the aroma analysis of wines.

EXPERIMENTAL

Winemaking. Sultaniye (*Vitis vinifera* L.) grapes of 2001 vintage were harvested at suitable maturity (21.5 Brix) from the Denizli province in the Aegean region of Turkey. Grapes were transported by a lorry to the Kavak1idere winery in 20 kg plastic boxes, crushed on a commercial grape crusher, and pressed in a pneumatic press (Dellatoffola–Italy), then 40 mg/L of sulfur dioxide was added. The juice (300 hl) was then settled at 12°C for 24 h in a stainless-steel tank. After settling, the juice was filtered by a diatomaceous earth rotary vacuum filter (Dellatoffola–Italy) and the turbidity of the juice was decreased to under 200 NTU. The juice was inoculated with *Saccharomyces cerevisiae* (Fermivin Arome-Gist Brocades-France) and fermented at 17°C. Upon completion of alcoholic fermentation, wine was racked and stored at 15°C for 6 month before analysis.

Extraction of Volatiles. SPME fibre (Supelco, Bellefonte, PA-USA) precoated with a 100 μm layer of polydimethylsiloxane (PDMS) was used. Two different SPME techniques were used in the extraction of the volatile aroma compounds: HS-SPME and a Im-SPME. Wine was saturated with sodium chloride for HS-SPME and a 50 mL sample for each extraction was placed into a 100 mL glass vial. In the HS-SPME analysis, PDMS fibre was inserted into the headspace of the glass vial, whereas in Im-SPME analysis, PDMS fibre was immersed into the sample and held in place for 30 min at 30°C.

During this time wine samples were stirred with a magnetic stirrer. After equilibration the fibre was removed from the sample and analytes were thermally desorbed in the injector port of the GC/MS instrument for analysis. Thermal desorption was performed in the injection glass liner at 250°C for 10 min. The analyses were carried out in triplicate.

GC-MS Analysis. Aroma compounds of the wine were analyzed by GC-MS. A Shimadzu QP 5050A apparatus equipped with CPSil5CB (25 m $\times$ 0.25 mm i.d., 0.4 µm film thickness) fused-silica capillary column was used. The flow rate of helium as a carrier gas was 1 mL/min. The injector temperature was at 250°C, set for splitless injection. Column temperature was 60°C//5°C/min//260°C for 20 min. MS were taken at 70 eV. Mass range was between *m/z* 30–425. A library search was carried out using the Wiley GC-MS Library and in-house Baser Library of Essential Oil Constituents. The MSs were also compared with those of reference compounds and confirmed with the aid of retention indices from published sources. The relative percentage amounts of the separated compounds were calculated from total ion chromatograms by a computerized integrator.

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