Methanol and Major Volatile Compounds of Turkish Raki and Effect of Distillate Source

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ABSTRACT

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Turkish Raki is the traditional anise flavoured distillate beverage produced mainly from a grape distillate called *suma*. Two types of Raki are produced in Turkey according to the distillate source. They are Type I – a fresh grape Raki produced only from *suma* and Type II – a Raki produced from a blended distillate of *suma* and alcohol of agricultural origin (mainly molasses). In this study the content of ethanol, methanol, distillate based major volatile compounds (aldehydes, esters, higher alcohols), aniseed based anethole and estragole, volatile acid and sugar values in two types of commercial Raki samples (40 samples) was determined and the effect of distillate source on the composition was examined. The distillate and the aniseed based major compounds of the Raki samples were analysed by direct injection with a GC-MS-FID according to the European Commission Reference Method. The results of variance analysis and PCA showed that there was a significant difference between the two types of Raki samples. Total volatiles (esters and higher alcohols), methanol, trans-anethole, estragole and sugar values were higher in the samples made from *suma* alone. All of the analysed component levels of the Turkish Raki samples were in compliance with Turkish Distilled Beverage Regulations. The methanol levels ranged between 28.00–50.87 g/hL absolute alcohol (AA) in Type I samples and 22.03–41.06 g/hL AA in Type II samples. Distillate based total volatiles levels ranged between 136.12–147.88 g/hL AA, with a mean value of 142.88 g/hL AA, in Type I samples and 102.44–113.45 g/hL, with a mean value of 107.9 g/hL, in the Type II samples. The anise based compound trans-anethole levels were significantly higher in the Type I samples (1,298–1,570 mg/L) than in the Type II samples (1,014–1,199 mg/L). According to distillate based volatiles, the Turkish Raki has a valuable content of volatile substances compared to other anise flavoured spirits.

Key words: anethole, distillate source, methanol, *suma,* Turkish Raki, volatile compounds.

INTRODUCTION

Turkish Raki is the traditional anise-flavoured distilled alcoholic beverage produced mainly from the grapes in Turkey. After beer, Raki is the most produced and consumed alcoholic beverage in Turkey, with a production of 45,000 kilolitres in 2008[24]. Raki is traditionally consumed either neat, or mixed with cold water and served with ice in a special long glass. Until 2004, Raki was produced under licence of the Turkish monopoly with no competition. After privatisation of the Monopoly in 2004, with increased competition from the private sector, several new brands and types of Raki have emerged, each with its own distinct composition and production method, although the overall qualities of the drink have generally been kept consistent. In recent years, alcoholic beverages have been subject to a high rate of taxation in Turkey and for this reason there is a great difference between the cost and sales price of these beverages. This has made counterfeit beverage production attractive. In 2005, 23 people died in Turkey and dozens were hospitalised after drinking counterfeit Raki containing lethal levels of methanol. Therefore, it became very important to control the quality of alcoholic beverages produced in Turkey. The Turkish Food Codex Distilled Alcoholic Beverage Regulation[23] of 2005, which allowed harmonization of Turkey with the European Community (EC) under the 1576/89 regulation[10], established the definition and production procedures for all distilled alcoholic beverages and fixed common analytical composition limits to control their quality and safety.

The distinctive volatiles, which gave characteristics to distilled alcoholic beverages, are affected by many variables such as raw material, flavour additives, and the processing steps, which include fermentation, distillation and aging[5]. The level of methanol and the main volatile compounds (higher alcohols, esters, aldehydes, volatile acids) of distilled beverages are one of the most important quality and safety factors that should be known and controlled by producers and legal authorities using EC reference methods (EEC2870/2000)[8]. According to the regulation EC 1576/89[10] and the Turkish Distilled Beverage Regulation[23], volatile substance content means the quantity of volatile substances (sum of the concentration of aldehydes: acetaldehyde and acetal; esters: ethyl acetate and methyl acetate; higher alcohols: 2-butanol, 1-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol; and volatile acids) other than ethanol and methanol contained in a spirit drink obtained by distillation of the raw material used.

According to the Turkish Distilled Alcoholic Beverage Regulation (2005/11)[23], Turkish Raki is produced by a second distillation with only *suma* (which is the distillate originating from grapes/raisin that is distilled to approximately 94.5% v/v alcohol with the purpose of keeping the flavour and smell of grapes) or *suma* mixed with ethyl alcohol (96% v/v) having an agricultural origin with anise

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seed (*Pimpinella anisum*) in traditional copper distillers (pot still) having a volume of 5,000 litres[3]. During the second distillation with anise seed, the medium and last product is separated and the medium part is used for Turkish Raki production. The alcohol concentration of the medium part is diluted with water to 45% (v/v). At the end of production, sugar is added and then the Raki is stored in oak barrels for a short maturation process (20–60 days)[25]. Apart from Turkey, there are some other anise-flavoured spirit drinks produced in European countries such as Pastis in France, Anis and Cazalla in Spain, Ouzo in Greece, Sambuca in İtaly and Janezevec in Slovenia (EC No 1576/89)[10]. The common feature of these spirit drinks is the use of nearly pure ethyl alcohol of agricultural origin (96% v/v) and the flavouring with a natural extract of anise, star anise, fennel or any other plant which contains the same principal aromatic constituents (EC 110/2008)[11]. Turkish Raki is quite different from the other anise-flavoured spirit drinks in terms of production, as only based distillate (*suma*) and anise (only *Pinpinella anisum* seed) are used. The Turkish Distilled Alcoholic Beverage Regulation[23] defines some special characteristics of Turkish Raki which are as follows. (1) Turkish Raki should be produced in Turkey. (2) For Raki production, either mainly fresh grape or raisin based ethyl alcohol called *suma* should be used and *suma* should be distilled up to 94.5% (v/v) alcohol with a continuous still to prevent the loss of aromatic compounds. At least 65% of the total distillate by volume in the second distillation should be *suma*, 35% of the total distillate can be agricultural based alcohol. (3) The amount of anethole of the etheric oil originating from the anise seed should comprise a minimum of 800 mg/L in the product. (4) During preparation, refined white sugar (sucrose) should be used and the amount of sugar should have a maximum of 10 g/L in the product.

Another important specific characteristic of Turkish Raki is the second distillation (pot still), which is performed with the presence of aniseed, instead of an anise extract addition. Today, principally there are two types of Raki production in Turkey according to the distillate source used. One type, the fresh grape Raki produced from *suma* alone (Type I), and the second type, the Raki produced from a blended distillate of *suma* (65%) and agricultural origin ethyl alcohol (max. 35% and mainly molasses alcohol) (Type II).

Since there had been a monopoly, there was limited research available on the volatiles of Turkish Raki and until now, there have been no studies on the effect of the alcohol source on Raki composition. The first objective of this study was to determine the average concentration and range of variation of methanol and the major volatile compounds of Turkish Raki by GC and GC-MS with direct injection according to EC reference method (EC2870/2000)[8]. The second objective was to compare the concentration of the volatiles and general composition between the two types of Raki.

MATERIALS AND METHODS

Samples

A total of forty Raki samples (75 cl each) belonging to 10 different brands produced by five well-known manufacturers in Turkey were selected. Twenty of these were the *suma* alone origin (Type I) denoted as fresh grape Raki and twenty were from the *suma* and agricultural based alcohol origin (Type II). Each brand consisted of four samples. Two of the four samples of each brand were collected from manufacturing plants and the rest were purchased from the local marketplace. The samples were stored at 5°C until analysed. All samples were injected in triplicate.

Reagents

The following standards were used (CAS number in parenthesis): acetaldehyde (75-07-0), acetal (1,1-diethoxyethane) (105-57-7), ethyl acetate (141-78-6), methyl acetate (79-20-9), methanol (67-56-1), 2-butanol (78-92-2), 1-butanol (71-36-3), 2-methyl-1-butanol (active amyl alcohol) (137-32-6), 3-methyl-1-butanol (isoamyl alcohol) (123-51-3), 3-pentanol (as internal standard) (71-41-0), estragole (4-allylanisole) (140-67-0), menthol (internal standard for anethole) (89-78-1) from Merck (Germany). The compounds 1-propanol (71-23-8), 2-methyl-1-propanol (isobutanol) (78-33-1), and trans-anethole (4180-23-8) were from Sigma (USA). The purity of all chemicals was above 98%. The stock solutions were prepared in ethanol/water (40% v/v). All other chemicals used were analytical grade and commercially available. Water was purified with a Millipore system (Millipore, Molsheim-France).

Analytical methods

Analysis of methanol and volatile compounds by GC and GC-MS. The major volatiles in the Raki samples were determined by direct injection into a GC using an internal standard method according to the EC reference method[8]. The internal standard used was 3-pentanol. A 9 mL aliquot of sample was mixed with 1 mL of an internal standard solution (243 mg/100 mL in 40% ethanol). Then 1 µL of the above mixture was injected into the GC.

The GC unit used was an Agilent 6890N, equipped with a flame ionization detector (FID). The separation column was a CP-WAX 57CB WCOT fused silica column (polyethylene glycol stationary phase, 60m x 0.25 mm i.d. with 0.4 µm film thickness; Chrompack, Netherlands). Injections were made in split mode (split ratio 50:1). Injection port temperature was 160°C and the oven was programmed 4 min at 40°C, from 40 to 92°C at 1.8°C/min, from 92 to 180°C at 30°C/min, then held for 4 min[13]. The FID temperature was 180°C (H_2: 30 mL/min and air: 300 mL/min). The carrier gas was helium with a flow rate of 1.3 mL/min. The identification of congeners was determined by comparing the retention times with those of authentic compounds. Analyses were carried out in triplicate and their averages were calculated. For the GC-MS analysis, an Agilent 6890N gas chromatograph was coupled to an Agilent 5975B VL MSD quadrupole mass detector. The separation column, the GC parameters and the column temperature program were the same as those described for the GC analysis. Transfer line, ion source and quadropole temperature were respectively 260°C, 250°C and 120°C. The electron impact (70ev) spectra were recorded at 1 s/scan with a scan range of 28–350 uma. Identification was performed by comparing the MS spectra with those of the Wiley and Nist database and with those obtained with pure standard compounds. A chromatogram of the standard compounds is given in Fig. 1. Identification and validation parameters of the method were detailed in Table I.

The concentration of each congener was determined with respect to the internal standard from the relative response factors (RRF), which were obtained during calibration under the same chromatographic conditions as those of the Raki analysis. The RRF for each compound was calculated using equation (1).

$$RRF = (A_{is} / A_c) \times (C_c / C_{is}) \quad (1)$$

where:

C_c: Concentration of compound (mg/100 mL)
C_{is}: Concentration of internal standard (mg/100 mL)
A_c: Peak area or height of compound
A_{is}: Peak area or height of internal standard

The results were calculated using equation (2) and expressed as g/hL in absolute alcohol.

$$C_c = (A_c \times A_{is}) \times C_{is} \times RRF \times (100/H) \quad (2)$$

where:

H: Alcoholic strength of sample

Trans-anethole and estragole analyses by GC. Trans-anethole and estragole contents of Raki samples were determined by direct injection (with the internal standard method) using a GC equipped with a FID and a CP-WAX 57CB WCOT fused silica column (polyethylene glycol stationary phase, 60 m × 0.25 mm i.d. with 0.4 µm

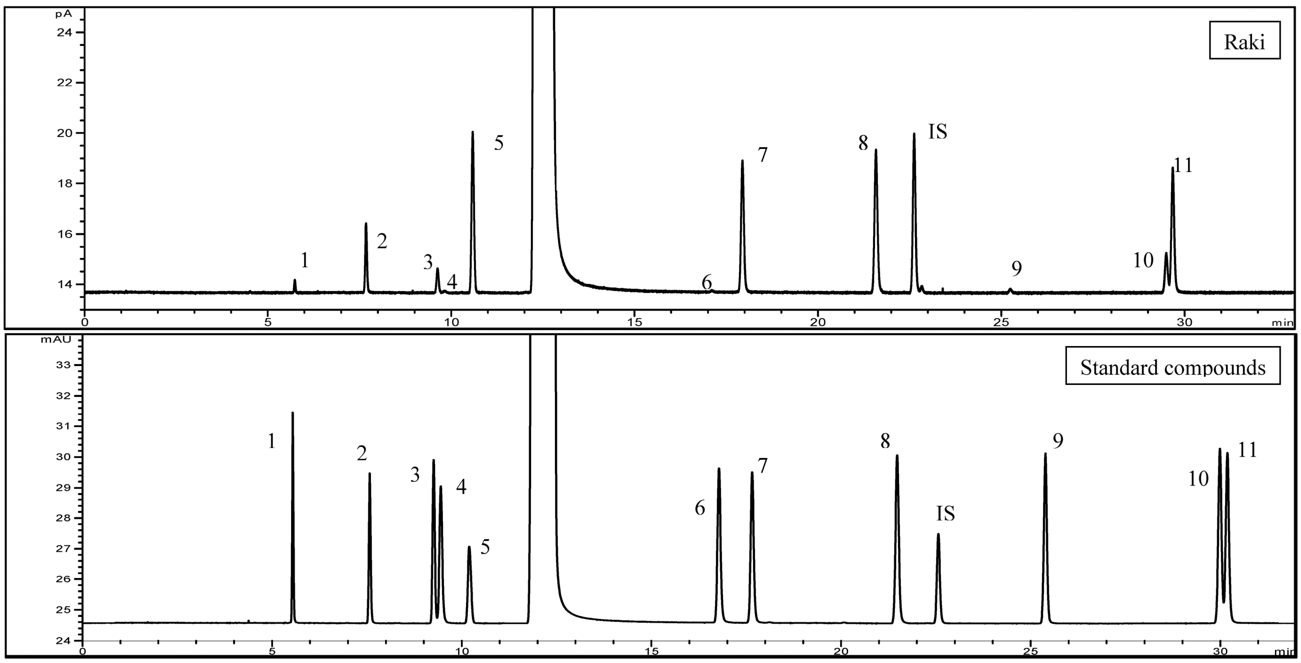

Fig. 1. Chromatograms of the standard compounds and Turkish Raki. Peak identification (1) acetaldehyde; (2) methyl acetate; (3) ethyl acetate; (4) acetal; (5) methanol; (6) 2-butanol; (7) 1-propanol; (8) 2-methyl-1-propanol; (IS) 3-pentanol (internal standard); (9) 1-butanol; (10) 2-methyl-1-butanol; (11) 3-methyl-1-butanol.

Table I. Identification and validation parameters for the analysis of methanol and volatile compounds.[a]

	Calibration curve (n = 9)							
Compounds	**Linearity range (mg/100 mL)**	**Slope (a)**	**Intercept (b)**	**R^2 [b]**	**LOD (s/n, 3:1) (mg/100 mL)[c]**	**RI[d]**	**ID[e]**	**Recovery range (average in %)**
Acetaldehyde	0.200–20.020	0.4973	–0.0008	0.9998	0.100	500	MS, RI	97.94
Methyl acetate	0.261–26.060	0.3842	–0.0017	0.9999	0.261	860	MS, RI	97.51
Ethyl acetate	0.264–26.390	0.5182	–0.0008	0.9999	0.176	895	MS, RI	100.10
Acetal	0.241–24.410	0.4207	–0.0045	0.9981	0.362	900	MS, RI	101.13
Methanol	1.155–46.184	0.4548	–0.0034	0.9999	0.277	905	MS, RI	100.63
2-butanol	1.186–47.440	0.8478	–0.0092	0.9999	0.109	1011	MS, RI	98.48
1-propanol	1.153–46.100	0.8257	–0.0098	0.9999	0.173	1042	MS, RI	99.10
2-methyl-1-propanol	1.191–47.620	0.9703	–0.0109	0.9999	0.159	1108	MS, RI	98.67
1-butanol	1.200–48.000	0.9191	–0.0107	0.9999	0.144	1138	MS, RI	98.87
2-methyl-1-butanol	1.171–46.820	0.9912	–0.0098	0.9999	0.140	1206	MS, RI	99.55
3-methyl-1-butanol	1.162–46.460	1.0273	–0.0125	0.9999	0.139	1206	MS, RI	99.45

[a] Regression equation: $y = ax + b$, where y is the peak area and x is the concentration mg/100 mL.
[b] R^2, correlation coefficient.
[c] Limit of detection: calculated by signal-to-noise ratio.
[d] Relative retention indices on DB-WAX column calculated against n-alkanes (C10–C16).
[e] Identification. MS, RI, identified on the basis of both mass spectral and GC retention index data.

film thickness; Chrompack, Netherlands) according to EC reference method[8]. Injections were made in split mode (split ratio 70:1). Menthol was used as the internal standard. The injection port and FID temperature was 230°C (H_2: 30 mL/min and air: 300 mL/min). The oven was kept at 180°C (isothermal). The carrier gas was helium with a flow rate of 2 mL/min. Analyses were carried out in triplicate and averages calculated. The sample amount injected was 1 μL. The concentration was determined with respect to the internal standard from the RRF. The results were expressed as g/L.

Other analyses. Raki samples were analysed for alcoholic strength by volume (pycnometry), volatile acidity (as acetic acid) and total sugars according to the EC reference methods for the analysis of spirits drinks (2870/2000)[8], neutral alcohol (1623/2000)[9] and wine (2676/90)[11].

Statistical analysis

The statistical methods used for the data analysis were analysis of variance (ANOVA). Furthermore, principal component analysis (PCA) was performed on the main volatile compounds to determine differences in the two groups of Raki samples. SPSS for Windows (version 15.0, SPSS Inc., Chicago, USA) was used for data processing.

RESULTS AND DISCUSSION

Ethanol and methanol content of Turkish Raki

Minimum, maximum and average values of ethanol and methanol compositions of Turkish Raki samples are given in Table II. The ethyl alcohol content of the Raki samples ranged between 44.95% (v/v) and 50.03% (v/v) and there was no significant difference between the two types of Raki. The ethanol content of the Raki samples were within the limits established by Turkish Distilled Alcoholic Beverage Regulation (2005/11)[23]. According to this regulation, the alcohol content of Turkish Raki should be at minimum 40% (v/v). All the samples had around a 45% (v/v) alcohol content, except for the two brands produced from *suma* (around 50% v/v). Yavas and Rapp[25] reported that some Raki produced from *suma* had an ethyl alcohol content of 50% (v/v).

Methanol is not a direct fermentation by-product, but is formed from pectin by pectolytic enzymes that hydrolyse the methoxyl group[4,15]. Although methanol is not one of the main volatile compounds of the distilled beverage, the control of methanol content is very important, because of its toxicity[2,21]. According to the Turkish Alcoholic Beverage Regulation (2005/11)[23], Turkish Raki must have a methanol level lower than 150 g/hL absolute alcohol (AA). The methanol levels of the Raki samples were found to be much lower than this limit, varying from 22.03 to 50.87 g/hL AA (Table II). With regard to the mean levels, methanol was higher in the samples made from *suma* and there was a significant difference between the two types. The methanol levels of the Turkish Raki samples were much lower than the levels presented for grape distilled beverages such as Portuguese Bagaceria (with a mean value of 753 g/hL AA), Italian Grappa (with the mean value of 1,216 g/hL AA), Spanish Orujo (with the mean value of 889.6 AA) and Greek Tsipouro (60.1–143.9 g/hL AA)[2,6,21]. However, the methanol content of the studied samples was higher compared to that of aniseed flavoured French Pernod[25]. Overall, Turkish Raki has a low level of methanol in relation to other grape based distilled beverages.

Volatile acid content of Turkish Raki

Volatile acids in distilled beverages are the volatile carboxylic acids and fatty acids[21]. Because more than 90% (v/v) of the total volatile acidity is acetic acid, they are expressed as acetic acid in the distilled beverage. They are formed during fermentation and storage of the spirit under inadequate conditions[7,21]. During distillation, they are entrained with the alcohol and their presence at a high level in the distillate has a negative effect on the sensorial qual-

Table II. The levels of ethanol, methanol and major volatile compounds of Turkish Raki (g/hL AA).

	Type I (Raki made from *suma*)			Type II (Raki made from *suma* and agric. origin alcohol)			
Compounds (g/hL AA)	**Min**	**Max**	**Mean ± sd**	**Min**	**Max**	**Mean ± sd**	**Sig.**
Ethanol %, v/v	44.95	50.03	47.00 ± 2.75	45.00	45.15	45.09 ± 0.06	ns[a]
Methanol	28.00	50.87	43.41 ± 9.23	22.03	41.06	30.50 ± 8.97	*[b]
Volatile acidity (as acetic acid)	1.35	2.79	1.82 ± 0.59	1.00	2.23	1.72 ± 0.48	ns
Aldehydes							
Acetaldehyde	0.96	3.19	2.22 ± 0.81	2.54	3.91	3.21 ± 0.63	*
Acetal	0.27	0.58	0.43 ± 0.13	0.35	1.35	0.63 ± 0.41	ns
Esters							
Methyl acetate	0.44	3.52	1.15 ± 1.33	0.25	1.40	0.70 ± 0.49	ns
Ethyl acetate	5.93	11.10	9.13 ± 2.01	5.00	15.50	8.61 ± 4.16	ns
Alcohols							
2-butanol	nd[c]	0.39	0.19 ± 0.17	nd	0.38	0.07 ± 0.16	ns
1-propanol	23.84	59.67	38.55 ± 13.10	20.69	52.24	30.37 ± 12.78	ns
2-methyl-1-propanol	30.24	54.88	45.93 ± 9.27	19.81	42.61	33.74 ± 8.58	*
1-butanol	0.78	1.59	0.97 ± 0.35	0.40	1.01	0.67 ± 0.26	*
2-methyl-1-butanol	8.28	14.69	11.71 ± 2.36	3.39	11.29	7.66 ± 3.94	*
3-methyl-1-butanol	22.57	57.72	30.93 ± 15.04	9.00	38.91	21.87 ± 13.11	*
Total volatile compounds[d]	136.12	147.35	142.88 ± 4.35	102.44	113.45	107.9 ± 54.26	*

[a] Not significant.
[b] $p < 0.05$
[c] Not detected.
[d] Total volatiles except ethanol and methanol, includes volatile acidity.

ity of the beverage. The volatile acidity of the Raki samples varied between 1.00 and 2.79 g/hL AA. As can be seen from Table II, Raki samples of Type II had a lower mean volatile acidity content compared to the samples of Type I. However, there was no significant difference between the two types of Raki. The volatile acidities of Raki samples were less than the levels that could have an adverse effect on quality.

Major volatile compounds of Turkish Raki

The major volatile compounds of both types of Turkish Raki are summarised in Table II. The concentrations of the volatiles are expressed as grams/hectolitre absolute alcohol (g/hL AA) according to European Regulation EC-2870/2000[8]. Differences between the two types of Raki samples are given, with a minimum, maximum and mean concentration of each compound. A characteristic chromatogram observed for Turkish Raki samples is presented in Fig. 1. The main volatile compounds detected in the Turkish Raki samples by the direct injection method were acetaldehyde, methyl acetate, ethyl acetate, acetal, methanol, 2-butanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol and 3-methyl-1-butanol, by the order of retention times.

Acetaldehyde is a compound that originates from fermented raw materials and increases during distillation and aging[16,20]. It is also formed as a result of spontaneous or microbial mediated oxidation. Acetaldehyde and acetal (or 1, 1-diethoxyethane) account for more than 90% of the total aldehyde content of the distilled beverage[21]. Acetaldehyde content in Raki samples analysed ranged between 0.96 and 3.91 g/hL AA. The mean concentration of acetaldehyde in the samples of Type I was significantly lower than that of the samples of Type II. High levels of acetaldehyde in Turkish Raki are usually associated with low quality, because of the low threshold values (0.0007–200 mg/L) and unpleasant odour[3]. Sensory descriptors for acetaldehyde range from nutty and sherry-like, to an odour reminiscent of overripe bruised apples[2]. Acetaldehyde levels in the Turkish Raki samples were lower than the levels reported for grape spirits such as Portuguese Bagaceria, Italian Grappa, Spanish Orujo and Greek Tsipouro[2,6,21].

Acetal or 1,1-diethoxyethane is a very common compound in distilled beverages and the major one among the acetals[16]. It is a colourless volatile compound with a pleasant smell at low levels that contributes to the flavour of alcoholic beverages[18]. Its threshold value is 0.0004–0.0042 g/hL AA[3]. Acetal levels in the Raki samples ranged from 0.27 to 0.58 g/hL AA with a mean value of 0.43 g/hL AA in the samples of Type I, and from 0.35 to 1.35 g/hL AA with a mean value of 0.63 g/hL AA in the samples of Type II. Although the mean level of acetal was lower in the samples made from *suma*, there was no significant difference between two types of Raki. Yavas and Rapp[25] reported higher values ranging between 0.90 and 7.80 g/hL AA in different types of Turkish Raki. Cortes et al. [6] reported a value of 1.39 g/hl AA acetal for Spanish Orujo.

Ethyl acetate is the most common ester compound in grape based distilled beverages and has an effect on the flavour properties of distillates, depending on its concentration[21]. It is well known that the proportion of ethyl acetate may be as high as 90% of the total ester content of distilled beverages[16]. Although ethyl acetate is unfavourable to distillate quality, giving a nail polish note at high concentrations (15–20 g/hL), it also contributes to fruity properties of beverages at low concentrations[2,3]. The esters detected in the Turkish Raki samples by direct injection were ethyl acetate and methyl acetate. The levels of ethyl acetate and methyl acetate in the Raki samples were in the range of 5.0–15.5 g/hL AA and 0.25–3.52 g/hL AA, respectively. Although, the results reflected a higher mean concentration of these compounds in the Raki samples of Type I, there was no significant difference between two types of Raki (Table II). The mean concentration of ethyl acetate has been reported to be from 44.4 g/hL to 853.8 g/hL AA for Portuguese Bagaceiras, Italian Grappa, Greek Tsipouro and Spanish Orujo[19,21,22]. In comparison to the mean values cited, Turkish Raki had the lowest ethyl acetate content among the grape based distilled beverages. However, some ethyl acetate levels of Raki samples were higher than those reported for Pernod and Ouzo (with a level of 1.1 and 0.94 g/hL AA, respectively). The ethyl acetate levels were consistent with those of Yavas and Rapp[25] but contradict with those of Anli et al.[1] in commercial Raki samples. The methyl acetate content reported for Orujo spirits was in the range of 1.23 and 8.65 g/hL AA[6].

The higher alcohols are formed by deamination and decarboxylation reactions from amino acids and sugars, during yeast fermentation[17]. They are quantitatively the most abundant group of volatiles in distilled beverages, especially in grape based spirits such as Grappa, Orujo, Tsipouro, Bagaceira[2,21]. Their level in the distilled beverages depends on the still type and technique used for distillation. Higher volatile levels and stronger flavours are promoted by use of pot stills, which do not fractionate volatiles as effectively as continuous stills[5]. The major higher alcohols which have been claimed to contribute favourable key notes to distilled beverages are 1-propanol, 2-methyl-1-propanol (isobutanol), 2-methyl-1-butanol (active amyl alcohol), 3-methyl-1-butanol (isoamyl alcohol) and 2-phenyl ethanol[21]. Higher alcohols are detectable organoleptically at concentrations below 15 g/hL of ethanol[14]. The most important higher alcohols detected by direct injection in Turkish Raki samples according to the mean concentrations were 2-methyl-1-propanol, 1-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol.

Among the higher alcohols, 2-methyl-1-propanol was the most abundant compound of the Raki samples with a range of 19.81–54.88 g/hL AA. Silva et al.[21] reported that 2-methyl-1-propanol was usually found at higher levels than 1-propanol and that the compound is claimed to contribute favourable notes to distilled beverages. The mean level of 2-methyl-1-propanol was significantly higher in Raki samples of Type I, than those of Type II ($p<0.05$). The 2-methyl-1-propanol levels of Turkish Raki samples were much higher (0.05 g/hL AA) than the levels reported for the other aniseed flavoured spirits such as French Pernod and Greek Ouzo, but lower than those reported for grape spirits such as Portuguese Bagaceria, Italian Grappa, Spanish Orujo and Greek Tsipouro[2,21,25].

The level of 1-propanol, the second most abundant compound in Turkish Raki samples, ranged between

20.69 and 59.67 g/hL AA. The compound has a pleasant, sweetish odour with the threshold value of 0.57–4.0 g/hL, but excessive levels can lead to solvent like negative notes in distillates[13,14]. Although the mean concentration of 1-propanol was higher in the Raki samples made from *suma* alone (Type I), there was no significant difference between the two types. The mean level of 1-propanol in the Raki samples was lower than those in grape distillates, but higher than those in Pernod and Ouzo[2,21,25].

The compounds 2-methyl-1-butanol and 3-methyl-1-butanol (amylic alcohol) with a sweet cooked and burnt odour are considered to be predictor of sensory character in the distilled beverage and lower levels are associated with a light-bodied grape distillate[21]. A high level of amyl alcohols has a negative effect on the flavour of distillate[2]. The 2-methyl-1-butanol and 3-methyl-1-butanol levels of the studied Raki samples were in the range of 3.39–14.69 g/hL AA and 9.0–57.72 g/hL AA, respectively. The amylic alcohol content of the Turkish Raki was lower than those reported for Bagaceria, Grappa, Orujo and Tsipouro and much higher than those reported for Pernod and Ouzo[2,21,25]. It was observed that each type of Raki sample showed a high variation according to the manufacturer. However the mean concentrations of 2-methyl-1-butanol and 3-methyl-1-butanol were significantly different between the two types. Their levels were higher in the samples made from *suma*. The levels of 3-methyl-1-butanol found in Turkish Raki contradict the values found by Anli et al.[1], whose data gave lower values than the present result.

The lowest higher alcohol detected by direct injection method in the Turkish Raki samples examined was 2-butanol. The difference between the two groups was not found significant. A high level of 2-butanol in distilled beverages is usually associated with low quality raw materials and an unpleasant flavour[21]. Another higher alcohol detected in the samples was 1-butanol. Its concentration ranged from 0.40 g/hL AA to 1.59 g/hL AA in the Raki samples. The mean concentration of 1- butanol in the samples of Type I was significantly higher than the mean concentration in the samples of Type II.

Turkish Distilled Alcoholic Beverage regulation (2005/11)[23] sets the minimum level of total volatile compounds other than ethanol and methanol for a series of distilled beverages. According to this regulation, the minimum level of the main volatile compounds of Turkish Raki must be equal to or exceed 100 g/hL AA. This is one of the most important quality control parameters of Turkish Raki in the marketplace. This level is conventionally considered to be equivalent to the sum of the concentration of aldehydes (as acetaldehyde and acetal), esters (as ethyl acetate and methyl acetate), higher alcohols (as 2-butanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol and 3-methyl-1-butanol) and volatile acids (as acetic acid). The concentration of the total volatile compounds of the Turkish Raki samples ranged from 102.44 to 147.35 g/hL AA. Comparing the two types, the volatile compound levels ranged between 136.12 and 147.35 g/hL AA with a mean value of 142.88 g/hL AA in the samples of Type I, and between 102.44–113.45 g/hL AA with a mean value of 107.9 g/hL AA in the samples of Type II. According to the total volatiles, the mean level of the Type I made from *suma* was significantly higher than that of the samples of Type II. Principal component analysis (PCA) was used to examine differences between the two types of Raki and the results are presented in Fig. 2. Evaluating the locations of the volatile compounds belonging to each brand of Raki samples, two groups formed. Component 1 and 2 explained 97.92% of the variance and indicated that there was a substantial difference between the two types according to the total volatile levels. These results compare well with those obtained from the ANOVA test.

Anethole and estragole content of Turkish Raki

The minimum, maximum and mean concentrations of trans-anethole and estragole in the Turkish Raki samples are presented in Table III. One of the important differ-

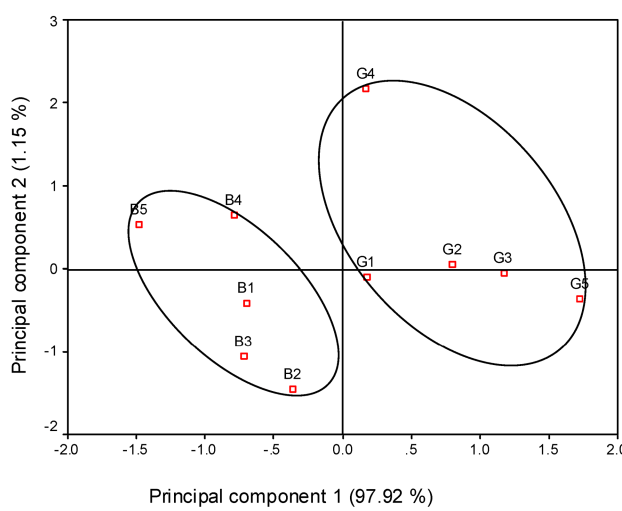

Fig. 2. PCA results for volatile compounds of the two types of Turkish Raki samples. G: Raki made only from *suma*. B: Raki made from *suma* and agriculture origin alcohol.

Table III. Trans-anethole, estragole, density and sugar content of Turkish Raki.

	Type I (Raki made from *suma*)			Type II (Raki made from *suma* and agricultural origin alcohol)			
	Min	Max	Mean ± sd	Min	Max	Mean ± sd	Sig.
Anethole (mg/L)	1,298.50	1,570.00	1,413.60 ± 93.08	1,014.50	1,199.00	1,126.60 ± 67.80	*[a]
Estragole (mg/L)	34.10	48.26	42.75 ± 4.59	27.50	37.15	34.82 ± 3.41	*
Density (g/cm^3)	0.9320	0.9408	0.9388 ± 0.05	0.9398	0.9410	0.9404 ± 0.001	ns[b]
Sugar (g/L)	4.20	5.95	5.70 ± 0.66	3.70	4.04	3.90 ± 0.56	*

[a] $p < 0.05$.
[b] Not significant.

ences in Turkish Raki compared to other aniseed flavoured distilled beverages is the direct use of aniseed *(Pimpinella anisum)* for Raki production, rather than its essential oil. The most abundant compounds giving an anise-like odour from the anise seed are trans-anethole, anisaldehyde and estragole with odour threshold values of 0.073, 0.047 and 0.016 mg/L, respectively[26]. Anise seed is added to the diluted grape distillate before the second distillation, using a pot still[25]. The trans-anethole and its isomer estragole were the major flavour compounds derived from aniseed and detected by the direct injection method. The trans-anethole content of Turkish Raki is especially important in terms of quality as it gives the characteristic flavour to the Raki. Trans-anethole levels of studied Turkish Raki samples of Type I and Type II ranged from 1,298.5 mg/L to 1,570.0 mg/L, with a mean value of 1,413.6 mg/L and from 1,014.5 mg/L to 1,199.0 mg/L with a mean value of 1,126.6 mg/L, respectively. The levels of trans-anethole was higher in the Type I Raki samples than those in the Type II, and there was a significant difference between the two groups ($p<0.05$). These findings were consistent with those of Yavas and Rapp[25] but contradict those of Anli et al.[1]. The trans-anethole levels in commercial Raki described by Anli et al.[1] were lower (under 5.8 mg/L) than the present levels. According to the Turkish regulations, the content of trans-anethole from aniseed in the Turkish Raki should be at minimum 800 mg/L[23]. It can be seen from Table II that both types of Raki were within that limit. The trans-anethole content of the studied Turkish Raki were lower than those reported for French Pernod (2,064 mg/L) and higher than those reported for Greek Ouzo (778 mg/L)[8,25]. The estragole content of the studied Raki samples ranged between 27.5 mg/l and 48.26 mg/L. The mean concentration of estragole in the Type I samples was significantly higher than the mean concentration in Type II. This is due to the higher amount of anise seed used in the *suma* based Turkish Raki production by the manufacturers.

Density values and sugar content of Turkish Raki

Table III shows the minimum, maximum and average values of density and sugar composition of the Turkish Raki samples analysed. The density ranged from 0.9320 g/cm^3 to 0.9408 g/cm^3 with a mean value of 0.9388 g/cm^3 in Raki samples of Type I and from 0.9398 g/cm^3 to 0.9410 g/cm^3, with a mean value of 0.9404 g/cm^3 in samples of Type II. The difference between two types was not significant. The density values of the Turkish Raki depend on their alcohol and sugar content.

The total sugar content of the Turkish Raki ranged from 4.20 to 5.95 g/L, with a mean value of 5.70 g/L in the samples of Type I, and from 3.70 g/L to 4.04 g/L with a mean value of 3.90 g/L in the samples of Type II. The mean concentration of sugar was higher in the samples made from *suma* than the samples of Type II, and there was a significant difference between two groups ($P < 0.05$). According to Turkish Distilled Alcoholic Beverage Regulation[23], the sugar must be white refined sucrose and the sugar content of Raki should not exceed 10 g/L. Traditionally at the end of Raki production, 6 g/L sugar is added to the Raki made from *suma* alone and 4 g/L for the Raki made from the *suma* and the agricultural origin ethyl alcohol[25]. Sahin and Ozcelik[18] reported the sugar content of seven Raki samples examined varied between 2.76–6.80 g/L.

CONCLUSIONS

The present study is the first attempt to compare the two types of Turkish Raki produced from *suma* alone and a blended distillate of *suma* and alcohol of agricultural origin in terms of the major volatile compounds, methanol and general composition. The results showed that the Turkish Raki composition was affected significantly by the Raki type. The total volatile compounds (aldehydes, esters, higher alcohols), methanol, trans-anethole, estragole and sugar values were found to be higher in Raki made from *suma* alone. The ethanol, total volatiles, methanol, trans-anethol and sugar content of all the analysed samples were within the legal limits according to Turkish Distilled Beverage Regulation[23]. The concentration of the total volatile compounds was higher than 100 g/hL AA in all of the studied Raki samples. Trans-anethole levels were higher than 1,000 mg/L in all of the samples.

In conclusion, to standardize and to gain international recognition and a geographical indication for traditional Turkish Raki, especially its special characteristics, the process (raw materials, fermentation, and distillation), reputation, quality factors and principal differences from other distilled beverages should be clarified with further studies.

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