Journal of Food Technology 10 (3): 87-91, 2012
ISSN: 1684-8462

Composition of Bogma Raki, Turkish Traditional Alcoholic Beverage

[1]Cem Zeren, [3]Zeki Aydin, [2]Zafer Yonden and [3]Serbay Bucak
[1]Department of Forensic Medicine,
[2]Department of Biochemistry, Faculty of Medicine,
[3]Department of Chemistry, Faculty of Art and Science,
Mustafa Kemal University, Hatay, Turkey

Abstract: Illegal alcohol consumption is one of the important public health problem in Turkey/Hatay, same as in the world. Researchers investigated the compositions of The Turkish traditional homemade raki is called Bogma raki which produced from grapes, figs or plums by GC/MS System. Commercial products and Bogma raki samples were analyzed for the amounts of ethanol, methanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol (isobutanol) and 3-methyl-1-butanol (isoamyl alcohol). The highest alcoholic strengths were ranged from 21-71% vol. in the illegal alcohols while the commercial alcohols had a very uniform alcoholic strength around 41.5% vol. Additionally most of the samples contained detectable amounts of trans-anethole, isoamyl alcohol, butanol and 1-propanol. Compared to commercial raki samples we have found substantial differences in the amounts of methanol, higher alcohols and toxic effects of homemade alcoholic beverages. Researchers conclude that this study is giving us significant data about the volatile components of illegal alcoholic beverage, Bogma raki in this region.

Key words: Illegal alcohol, ethanol, methanol, Bogma raki, region, volatile

INTRODUCTION

Illegal alcohol consumption is one of the most important public health problem in Turkey, same as in the world (Lachenmeier *et al*., 2009a; Lang *et al*., 2006; Narawane *et al*., 1998; Popova *et al*., 2007). The illegal alcohol term has multiple definitions; it can be classified under four major categories: illegally produced alcohol, surrogate alcohol, i.e., non-beverage alcohol such as perfume and medicine, alcohol not registered in the country where it is consumed and legal unregistered alcohol (e.g., homemade alcohol in countries where it is legal) (Lachenmeier *et al*., 2009b, 2011). According to World Health Organization (WHO) the 30% of global alcohol consumption comes from unrecorded sources (Table 1) (WHO, 2010) where the highest consumption of unrecorded alcohol is in Europe, South America and Africa, respectively. The consumption rate of unrecorded alcohol in Ukraine was about 50%, in 2005 (Lachenmeier *et al*., 2010) (Table 1). As well as surrogate alcohol that is not officially intended for human consumption.

In Turkey, raki is the national hard alcoholic drink and it is similar to several other alcoholic beverages available around the Mediterranean, the Middle East and in Colombia, e.g., pastis, ouzo, sambuca, arak and aguardiente. Raki is produced by the official industries of the state and it is also produced at home illegally by the people who live in the villages, in Cukurova region, especially in Hatay, a border city nearby Syria. This Turkish traditional homemade raki is called Bogma raki (Arabic name, Arak tini) and it is produced from grapes, figs or plums. Because of its low cost and special taste, some people especially prefer to consume Bogma raki. The price of this kind of beverage is fivefold cheaper than commercial products. The homemade producers generally use their own traditional methods so the ingredients are so different from official rakis and also from each other. For that reason the compositions of these alcoholic beverages are not standard for ethanol, methanol and other ingredients. Because of its price people consume Bogma raki in huge amounts and this cause serious intoxication. The deaths due to alcohol intoxication are also frequently seen in legal autopsies (Azmak *et al*., 2002; Bilgin *et al*., 2000).

The consumption of Bogma raki is too much in the region and there is no literature on the composition of Bogma raki even for the most basic parameters such as alcoholic strength. Researchers aimed to enlighten the compositions of this traditional alcoholic beverage so this study will fill the gap about this field.

Corresponding Author: Cem Zeren, Department of Forensic Medicine, Faculty of Medicine, Mustafa Kemal University, 31100 Hatay, Turkey

Table 1: Global distribution of unrecorded adult per capita alcohol consumption 2005 own calculation based on WHO

WHO region	Unrecorded adult per capita alcohol consumption in l pure ethanol	Total adult per capita alcohol consumption in l pure ethanol	Proportion unrecorded (%)
Africa	1.93	6.19	31
America	2.01	8.70	23
Eastern Mediterranean region	0.34	0.62	55
Europe	2.67	12.20	22
South East Asia region	1.52	2.24	68
Western Pacific region	1.63	6.23	26
World	1.75	6.13	29

MATERIALS AND METHODS

Sampling: Commercial products were purchased from a variety of stores and Bogma raki samples were obtained from local markets and from individuals who made their own beverages for personal usage. Samples of each product were decanted into sterile glass bottles.

Analysis of products: Ethanol, methanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol (isobutanol) and 3-methyl-1-butanol (isoamyl alcohol) were used as standards for qualitative and quantitative analysis of spirits. All chemicals were of analytical grade and were supplied by Merck (Darmstadt, Germany). The spirits were analyzed on a Hewlett-Packard (Palo Alto, CA) GC/MS system consisting of an HP 6890 gas chromatograph, an HP 5972 Mass Selective Detector (MSD) and an HP 6890 automatic liquid sampler. Separations of spirits compounds of methanol, ethanol, 2-butanol, 1-propanol, 1-butanol and isoamyl alcohol were accomplished by using an HP-FFAP (25 m×0.2 mm i.d., 0.33 μm film thickness) cross-linked capillary column (Hewlett-Packard Co., Palo Alto, CA).

The GC/ MS parameter; the pressure of the carrier gas helium was 6.0 bar and the split value with a ratio of 1:100. The injection unit temperature set to 250°C and MS quadrupole temperature set to 280°C. The MS quadrupole detector ionization energy set to 70 eV. The initial column temperature was 60°C (for 4.0 min) programmed by 6°C min^{-1} to final temperature 160°C and kept for 4 min at 160°C.

A comparison between the retention times of the samples with those of authentic standard mixture (Merck, Darmstadt, Germany; 99.9% purity specific for GLC), run on the same column under the same conditions is made to facilitate identification. After that all spirits chromatograms verified by accessing Wiley database.

RESULTS AND DISCUSSION

The composition for the most important compounds is shown in Table 2 (v/v). A total of 81 samples were collected and analyzed. The alcoholic strengths of the samples ranged from 21-71% vol. The highest alcoholic strengths were typically found in the illegal alcohols while the commercial alcohols had a very uniform alcoholic strength around 41.5% vol. however, in many of the samples trans-anethole, isoamyl alcohol, butanol and 1-propanol found at detectable amounts. The home-made raki (Bogma raki) showed a higher variation in alcoholic strengths with a similar mean at around 45% vol. and the variances of alcoholic strength in homemade raki depended mostly on the preferences of producers who usually make it for personal use and may add other ingredients such as plump, grape or anise (*Pimpinella anisum*) in order to change the taste.

Methanol was detected in 45 of 69 illegal raki samples but not detected in commercial samples. Concentrations of methanol were ranging from undetectable to 284.4 g hL^{-1} of pure alcohol (g hL^{-1} pa). Means of the methanol concentrations is 98.30±101.53 g hL^{-1}.

Isoamyl alcohol, butanol and 1-propanol were called as higher alcohol. Isoamyl alcohol concentrations were ranged from undetectable to 1028 g hL^{-1} of pure alcohol (g hL^{-1} pa) and the mean isoamyl alcohol concentrations of illegal Bogma raki and commercial raki samples are 447.43±261.84 and 187.83± 80.95 g hL^{-1}, respectively.

Among the illegal samples analyzed, the ethyl acetate content for 45 samples was below the detection limit and for 39 samples was above 100 g hL^{-1} pa. Particularly noticeable, a sample's ethyl acetate concentration was extremely high (1,809 g hL^{-1} pa).

The acetic acid concentrations of the illegal samples were varied between non-detected to 1669.0 g hL^{-1} pa (mean: 125.76±296.55 g hL^{-1} pa) however no acetic acid was detected in legal raki samples.

The trans-anethole concentrations of the illegal samples were so different between each other and were varied between non-detected and 2415.9 g hL^{-1} and in legal samples the anethole concentrations were varied between 1494.9 and 1930.5 g hL^{-1}.

None of the illegal or commercial raki samples contained ethyl carbamate above the detection limit. Illegal alcohol poisoning deaths are important in forensic

Table 2: Chemical composition of illegally produced raki samples in comparison with data from legal raki samples

Raki sample	N	Minimum	Maximum*	Mean*	SD
Illegal					
Trans-anethole	69	ND	2415	865	754.0
Acetic acid	69	ND	1669	126	297.0
Methanol	69	ND	284	98.3	102.0
Isoamyl alcohol	69	ND	1028	447	262.0
Butanol	69	ND	793	92.5	120.0
1-propanol	69	ND	149	35.1	42.1
Ethyl acetate	69	ND	1809	325	443.0
Ethyl carbamate	69	ND	ND	ND	
Ethanol (% vol.)	69	21	71	45.2	11.2
Legal					
Trans-anethole	12	1494	1930	1664	156.0
Acetic acid	12	ND	ND	ND	
Methanol	12	ND	ND	ND	
Isoamyl alcohol	12	121	340	188	81.0
Butanol	12	81	243	126	61.9
Propanol	12	39	141	87.1	36.2
Ethyl acetate	12	ND	117	67.4	42.8
Ethyl carbamate	12	ND	ND	ND	-
Ethanol (% vol.)	12	39	46	42.0	2.7

*g hL^{-1} pa; ND: Not Detected

science. It was estimated that deaths due to methanol intoxication were merely 4.6-8.25% among all intoxications (Bilgin *et al*., 2000). Poisoning cases due to methanol is very frequent in the region. This study has identified the amount of volatile compounds in illegal rakis including methanol. In one of the earlier studies methanol poisoning in Edirne-Turkey has been investigated (Azmak *et al*., 2002) and it has shown that the rate of deaths due to methanol poisoning was 3.36% of all forensic death cases. According to the Estonian Bureau of Forensic Medicine report the 11.8% of all fatal alcohol poisonings are attributed to consumption of surrogates. This equals around 23 deaths in Estonia each year and thus isn't likely to be an underestimate (Lang *et al*., 2006).

Illegal raki samples, in terms of ethanol concentration, showed high range variety against commercial raki samples. This is similar to other studies in which unrecorded alcohol contained higher alcoholic strengths than recorded alcohol. For instance, the results of a study that was made on Estonian surrogate alcohol (Lang *et al*., 2006) in which the mean concentration of illegally homemade alcohol (moonshine) was 42.8% vol. Similarly, McKee *et al*. (2005) found an average alcohol content of 38.9% vol. In Russian samogon (McKee *et al*., 2005) and in Poland, the unrecorded spirits typically contained around 48% vol. with some products as high as 71% vol. (Lachenmeier *et al*., 2009a, b).

Methanol is the substance most often associated with the toxicity of surrogate and other alcohols (Lachenmeier *et al*., 2007). In the study, the results for methanol in 45 samples were higher than EU limit of 30 g hL^{-1} pa for neutral alcohol. This can be explained by the use of fruits as a main component which was the major source for methanol in spirits. Methanol is commonly produced in fruit based spirits by the action of pectin esterase on pectin found in fruit (especially grapes and plumps), explaining its presence in home-produced alcohol. For that reason, the methanol limit for fruit spirits in the EU is set higher at 1000 g hL^{-1} pa[14]. However, the methanol content of the Ukrainian products was relatively low (i.e., lower than the EU limit of 30 g hL^{-1} pa for neutral alcohol) (European Parliament and Council, 2008) as well as lower than in recent studies of unrecorded alcohols from Poland (Lachenmeier *et al*., 2009a, b).

In the study, the concentrations of isoamyl alcohol, butanol and 1-propanol called higher alcohols varied considerably in raki samples between undetectable and 10280.7 g hL^{-1} pa (isoamyl alcohol). The EU limit of 1000 g hL^{-1} pa was exceeded by some of the samples.

The higher alcohol levels were higher than the levels of some previous investigations of home-produced spirits (as high as 1028.7 g hL^{-1} pa) (Lachenmeier *et al*., 2009a, b; Lang *et al*., 2006; Szucs *et al*., 2005). These types of alcohols, congeners at levels that have been shown in animal studies to cause hepatic damage compared the levels of glutamate pyruvate transaminase (EC: 2.6.1.2) and glutamate dehydrogenase (EC: 1.4.1.4) enzymes released from isolated rat livers perfused with solutions containing different types of these kinds of alcohols. High levels of glutamate dehydrogenase, indicates a more serious degree of hepatotoxicity, greater after exposure to 1-propanol, 1-butanol, 2-butanol, isobutanol and isoamyl alcohol (Strubelt *et al*., 1999).

The EU limit both for ethyl acetate and acetic acid is 100 g hL^{-1} pa (European Parliament and Council, 2008) and in the study 39 samples' concentrations were higher than EU limit. Particularly noticeable, a sample's ethyl acetate concentration was extremely high (1,809 g hL^{-1} pa). The acetic acid concentrations of the illegal samples were varied from non-detected to 1669.0 g hL^{-1} pa (mean: 125.76±296.55 g hL^{-1} pa) where as no acetic acid was detected in legal raki samples. This can be explained due to the bacterial contamination of homemade products because ethyl acetate and acetic acid are produced microbiologically from spoiled mash indicated concurrently with high concentrations of ethyl acetate and acetic acid (i.e., esters of the metabolites from ethyl acetate and acetic acid bacteria).

Trans-anethole-a flavoring that is generally recognized as safe by the US Food and Drug Administration has been shown to cause hepatotoxicity in different studies (Caldwell and Sutton, 1988; Newberne *et al*., 1989, 1999; Schulz *et al*., 2008). Continuous intake of high dose levels of trans-anethole has been shown to induce a continuum of cytotoxicity, cell necrosis and cell proliferation. In chronic dietary studies in rats, hepatotoxicity was observed. In female rats, chronic hepatotoxicity and a low incidence of liver tumors were reported at a dietary intake of 550 mg trans-anethole/kg body weight/day (Newberne *et al*., 1999).

The anethole concentrations detected in the German products lay in the region of 400-800 mg L^{-1}. The anethole concentration in the selected Greek products varies from 300-300 mg L^{-1} (Schulz *et al*., 2008). In the study the anethole concentrations of illegal samples were varied from not detected to 2415.9 g hL^{-1} and the anethole concentrations of legal samples were varied from 1494.9-1930.5 g hL^{-1}. According to the results, the anethole concentrations of illegal rakis are so similar at higher levels but so different at lower levels compared with legal raki samples however the anethole concentration of illegal raki samples are so variable because of homemade producers' preference of anise amounts.

As a result researchers can say, long-term dietary studies, not alone with trans-anethole but together with alcohol consumption will be much more useful to assess the hepatotoxicity of this agent. So, researchers may understand clearly the harmful effects of homemade Bogma rakis.

CONCLUSION

This current study is the largest study about homemade Bogma raki for the region and is one of the largest in the country. Compared with commercial raki samples researchers have found substantial differences in the amounts of methanol, higher alcohols and toxic effects of homemade alcoholic beverages. Currently, there is insufficient evidence to conclude that alcohol quality influences alcohol-attributable mortality rates over and above the effects of ethanol, aside from limited methanol outbreaks. Researchers found some evidence for potentially toxic concentrations.

Researchers conclude that this study is giving us significant data about the volatile components of illegal alcoholic beverage, Bogma raki, in this region. With the light of yhe results, it should be considered that this alcoholic beverage should be produced legally without carrying poisoning risks.

REFERENCES

Azmak, D., O. Erdonmez, G. Altun, C. Zeren and A. Yilmaz, 2002. Deaths due to methanol poisoning in Edirne; 13 cases report. Proceedings of the Annual Legal Medicine Meeting, May 16-19, 2002, Turkey, pp: 193-196.

Bilgin, N., N. Cekin, M.K. Gulmen, B. Alper, N. Kanat and B. Savran, 2000. A review of toxicological analysis of legal autopsy in Adana. Proceedings of the 4th Forensic Science Congress, May 10-13, 2000, Istanbul, Turkey.

Caldwell, J. and J.D. Sutton, 1988. Influence of dose size on the disposition of trans-[methoxy-14C]anethole in human volunteers. Food Chem. Toxicol., 26: 87-91.

European Parliament and Council, 2008. Regulation (EC) No 110/2008 of the European parliament and of the council of 15 January 2008 on the definition, description, presentation, labelling and the protection of geographical indications of spirit drinks and repealing Council Regulation (EEC) No 1576/89. Official J. Eur. Union, L39: 16-54.

Lachenmeier, D.W., A.V. Samokhvalov, J. Leitz, K. Schoeberl and T. Kuballa *et al*., 2010. The composition of unrecorded alcohol from eastern Ukraine: Is there a toxicological concern beyond ethanol alone?. Food Chem. Toxicol., 48: 2842-2847.

Lachenmeier, D.W., B. Sarsh and J. Rehm, 2009a. The composition of alcohol products from markets in Lithuania and Hungary and potential health consequences: A pilot study. Alcohol. Alcohol., 44: 93-102.

Lachenmeier, D.W., B.J. Taylor and J. Rehm, 2011. Alcohol under the radar: do we have policy options regarding unrecorded alcohol?. Int. J. Drug Policy, 22: 153-160.

Lachenmeier, D.W., J. Rehm and G. Gmel, 2007. Surrogate alcohol: What do we know and where do we go?. Alcohol. Clin. Exp. Res., 31: 1613-1624.

Lachenmeier, D.W., S. Ganss, B. Rychlak, J. Rehm, U. Sulkowska, M. Skiba and W.W. Zatonski, 2009b. Association between quality of cheap and unrecorded alcohol products and public health consequences in Poland. Alcohol. Clin. Exp. Res., 33: 1757-1769.

Lang, K., M. Vali, S. Szucs, R. Adany and M. McKee, 2006. The composition of surrogate and illegal alcohol products in Estonia. Alcohol. Alcohol., 41: 446-450.

McKee, M., S. Suzcs, A. Sarvary, R. Adany, N. Kiryanov, L. Saburova, S. Tomkins, E. Andreev and D.A. Leon, 2005. The composition of surrogate alcohols consumed in Russia. Alcohol. Clin. Exp. Res., 29: 1884-1888.

Narawane, N.M., S. Bhatia, P. Abraham, S. Sanghani and S.S. Sawant, 1998. Consumption of 'country liquor and its relation to alcoholic liver disease in Mumbai. J. Assoc. Phys. India, 46: 510-513.

Newberne, P., R.L. Smith, J. Doull, J.I. Goodman and I.C. Munro *et al*., 1999. The FEMA GRAS assessment of trans-anethole used as a flavouring substance. Flavour and Extract Manufacturer's Association. Food Chem. Toxicol., 37: 789-811.

Newberne, P.M., W.W. Carlton and W.R. Brown, 1989. Histopathological evaluation of proliferative liver lesions in rats fed trans-anethole in chronic studies. Food Chem. Toxicol., 27: 21-26.

Popova, S., J. Rehm, J. Patra and W. Zatonski, 2007. Comparing alcohol consumption in central and eastern Europe to other European countries. Alcohol. Alcohol, 42: 465-473.

Schulz, K., K. Schlenz, S. Malt, R. Metasch, W. Romhild, J. Dressler, D.W. Lachenmeier, 2008. Head space solid-phase microextraction-gas chromatography-mass spectrometry for the quantitative determination of the characteristic flavouring agent eugenol in serum samples after enzymatic cleavage to validate post-offence alcohol drinking claims. J. Chromatogr. A., 1211: 113-119.

Strubelt, O., M. Deters, R. Pentz, C.P. Siegers and M. Younes, 1999. The toxic and metabolic effects of 23 aliphatic alcohols in the isolated perfused rat liver. Toxicol. Sci., 49: 133-142.

Szucs, S., A. Sarvary, M. McKee and R. Adany, 2005. Could the high level of cirrhosis in central and eastern Europe be due partly to the quality of alcohol consumed? An exploratory investigation. Addiction, 100: 536-542.

WHO, 2010. Global Status Report Alcohol. World Health Organization, Geneva, Switzerland.