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COMPOSITION OF SURROGATE ALCOHOL FROM SOUTH-EASTERN NIGERIA

Obiora S. Ejim Enugu State University of Science and Technology (ESUT), Enugu, Nigeria

Bruna Brands Centre for Addiction and Mental Health (CAMH), Toronto, Canada

Jürgen Rehm Centre for Addiction and Mental Health (CAMH), Toronto, Canada

Dirk W. Lachenmeier

Chemisches und Veterinäruntersuchungsamt (CVUA) Karlsruhe, Karlsruhe, Germany

ABSTRACT

The quality of home brewed beverages (e.g., ogogoro) in Nigeria has been a source of concern for some time. However, the composition of these beverages remains largely unknown. In this pilot study samples of surrogate alcohol from the southeastern parts of Nigeria were analyzed for alcohol concentration, composition of volatile and non-volatile components and water quality. The results showed that the samples contained concentrations of alcohol that were in agreement with those previously reported for ogogoro. However, the concentrations of other components (e.g., methanol, lead) were well below those associated with acute toxic effects. One sample contained an unknown additive and was being sold as an 'antimalarial'. The implications of these findings are discussed.

KEY WORDS: KEY WORDS: surrogate alcohol, moonshine, quality of spirits, Nigeria

INTRODUCTION

Traditional alcoholic beverages have been consumed in Nigeria and other West African communities for centuries, and western commercial spirits, beer and wine have been available since pre-colonial days (Obot, 2007). African fermented foods were reviewed by Odunfa and Oyewole (1998). In many African countries, traditional spirits are obtained by the distillation of fermented local sugary substrates. However, information on these is hard to obtain since the production is illegal in many countries. Since colonial times the view is that the spirits may contain toxic alcoholic components due to lack of scientific quality control.

Corresponding author: Bruna Brands, PhD, Centre for Addiction and Mental Health, 33 Russell St., Toronto, Ontario, Canada M5S 2S1; tel. 416-535-8501 x6860; fax 416-595-6899; e-mail: Bruna_Brands@camh.net

Sample	1	2	3	4	5	6
Sampling site	Agbani, Enugu State	Ogbete Market, Enugu	Amokwe, Enugu	Presidential Road, Enugu	Presidential Road, Enugu	Kuje, Abuja
Description	Clear, colorless liquid without distinct smell	Clear, colorless liquid without distinct smell	Clear, colorless liquid without distinct smell	Clear, colorless liquid without distinct smell	Brown liquid with dark precipitation, sold as anti- malarial	Clear, colorles liquid without distinct smell

Table 1. Sample collective of Nigerian surrogate alcohol*

Ogogoro)

In West Africa, ogogoro (also known as kinkana and apetesi) is a spirit drink distilled from palm wine. In Nigeria, distillation takes place in small sheds dotted along the coastal areas and in villages across the South. The end product is a clear liquid with alcohol content often higher than 40%. The drink is stored in large plastic containers and transported to all parts of the country where it is sold in bottles. Consumers can also buy ogogoro in shots in drinking parlors. The production of ogogoro has risen sharply in Nigeria in recent years because it is used as the main ingredient in the production of commercial liquors. In what is a thriving market in fake brandy and whiskey today, the constituents of these drinks often turn out to be bad ogogoro and some coloring (Obot, 2000).

Besides anecdotal evidence and limited results from the 1980s (Odeyemi, 1980), there is no systematic information about the composition of Nigerian spirits available. We conducted this pilot study to obtain an up-to-date overview about Nigerian alcoholic beverages. For the first time, we have conducted a comprehensive analysis of ogogoro samples including alcoholic strength, volatile compounds, heavy metals, as well as water quality parameters. From those we aimed to identify the compounds occurring in toxic ranges that may be studied in more detail in a larger sample.

METHOD

Samples

Samples of surrogate alcohol (illegally produced and unrecorded) were obtained from retail outlets across the southeastern part of Nigeria. Aliquots (shots of about 50 ml) were purchased randomly from small retailers that serve the public in small gatherings, market squares, labour camps and/or lower cadre drinking parlors. The samples were poured directly into clean plastic vials collected from medical suppliers at the university. Contamination from other sources, e.g., water, was avoided. The small retailers had bought their supplies from major retailers who in turn had purchased them from the distillers. The distillations are done mainly in the Delta (Warri, Sapele and Burutu) and Rivers states of Nigeria. The source of raw material is presumably the sap from 'raffia palm'. The other sap of palm wine from the upland is more expensive and does not flow as much in quantity hence raffia palm wine is the most economic source for distillation. Any additive to the gin is done at the final retail outlet. The list of collection sites and a visual description of the samples is presented in Table 1.

Analytical procedure

Alcoholic strength and total dry extract were determined by Fourier transform infrared spectroscopy according to the method described

in Lachenmeier (2007). Volatile components were analyzed on the basis of the European Community reference methods for the analysis of spirits using gas chromatography (GC) with a flame-ionization detector (FID) (European Commission, 2000). Additional details on the GC-FID procedure are published elsewhere (Lachenmeier et al., 2006). Ethyl carbamate was determined using GC with tandem mass spectrometry (GC-MS/MS) (Lachenmeier et al., 2005). Anionic composition was analyzed using ion chromatography (Lachenmeier et al., 2003). Conductivity was measured using the procedure in Lachenmeier et al. (2007b). Inorganic elements were analyzed using semiquantitative inductively coupled plasma mass spectrometry (ICP-MS) after evaporation of the sample and re-constitution in ultra-pure water. Furthermore, all samples were screened for unknown substances using high-performance liquid chromatography with a diode-array detector (HPLC-DAD) and gas chromatography with mass spectrometry (GC-MS).

Reporting of results

Alcoholic strength is indicated by 'percent by volume' (% vol). Volatile compounds contained in each sample are expressed in the unit 'g/hl of pure alcohol' or 'g/hl of 100% vol. alcohol' (i.e., the concentrations are standardized in regard to the alcoholic strength) according to the procedure outlined in the European Community reference methods for the analysis of spirits (European Commission, 2000). This approach is superior because the samples can be directly compared irrespective of their individual alcoholic strength. For better clarity, we use the abbreviation 'g/hl p.a.'. The results for the non-volatile components are presented as 'mg/l'.

RESULTS

The results for alcoholic strength and volatile composition are outlined in Table 2. The alcoholic strengths of the sample were in the range between 32.2 and 42.6% vol. Methanol was detected in all samples in concentrations between 4.4 and 31 g/hl p.a. The content of higher alcohols encompassed a considerable range between 34 and 269 g/hl p.a. Two samples had a rather low content of higher alcohols (34 and 46 g/hl p.a., samples # 1 and 6), whereas the other samples had higher concentrations above 150 g/hl p.a. The same difference was found for the esters ethyl acetate and ethyl lactate, as well as for acetaldehyde.

Besides the substances shown in Table 2, we have quantitatively analyzed 1-hexanol, benzyl alcohol, benzyl acetate, benzaldehyde, ethyl benzoate, ethyl caprylate and methyl acetate. However, these substances were not detectable in any of the samples. Ethyl carbamate was also not detectable in any of the samples. Ethyl carbamate was also not detectable in any of the samples using GC-MS/MS. During the screening analyses for unknown substances using HPLC-DAD and GC-MS, no further toxicologically relevant substances were discovered. We were able to exclude quinine as the anti-malarial substance in sample 5, but could not spectrally assign a possible herbal medicine used for this regard.

All elements that were positively detected during our ICP/MS screening analysis for elemental composition are shown in Table 3. The most abundant elements with concentrations in the mg/l range were the alkali and alkaline earth metals sodium (2.5–54 mg/l), potassium (3.4–93 mg/l), calcium (0.8–3.8 mg/l), and magnesium (0.13–4.9 mg/l). Besides those, only copper was contained up to the mg/l range (0.01–3.7 mg/l). Other metals were found only in traces.

The conductivities of the samples ranged from 19 to 133 μ S/cm (Table 4). Chloride was detected in most of the samples (3.9–46.7 mg/l). Nitrate was positive in three samples (2.3–29.1 mg/l), sulfate in two (8.3–13.3 mg/), whereas phosphate was detected in only one of the samples (6.8 mg/l).

DISCUSSION

Strength of alcohol beverages

The alcoholic strengths of the samples were in good accordance with the range of 26.8 to

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							EU				
							maximum				
							level for				Legally
							neutral				distilled fruit
							alcohol/	Ogogoro	from	from	spirits
								from Nigeria	Tanzania	Russia	(Lachenmeier
Sample	1	2	3	4	5	6	spirits (EC, 1989)	(Odeyemi, 1980) ¹	(Mosha et al., 1996) ²	$(Nuzhnyi, 2004)^2$	and Mu β hoff, 2004) ²
Ethanol [%	32.2	42.4	42.6	37.6	37.4	37.0	-	24.5-40.3	21.0-44.0	(no data)	31.2-49.1
vol]											
Methanol [g/	4.4	31	20	18	18	5.6	50/1000	nd-9	20-38	0-164	25-1389
hl p.a.]											
Acetaldehyde [g/hl p.a.]	1.5	11	11	18	17	1.2	0.5/no limit	(no data)	0.5-8	1.3-212	(no data)
1-Propanol	24	37	28	29	30	32	-	nd-50	10-19	2-142	16-1393
[g/hl p.a.]											
1-Butanol [g/	nd	1.0	0.8	0.6	0.5	nd	-	(no data)	$50-200^{(3)}$	0-65	1-55
hl p.a.]											
2-Butanol [g/	0.5	2.6	3.8	3.3	3.5	nd	-	(no data)	(no data)	0-53	nd-368
hl p.a.]											
Isobutanol	5.6	48.8	28.0	26.0	26.4	2.1	-	33-153	(no data)	4.7-967	15-813
[g/hl p.a.]									<i>.</i>		
Amyl	5.2	175	101	93	94	nd	-	127-291	(no data)	9-1170	4-456
alcohols											
[g/hl p.a.]	0.5	4.4	3.7	2.8	2.8			(na data)	(na data)	0-38	(no doto)
2-Phenyl ethanol [g/	0.5	4.4	3.7	2.8	2.8	nd	-	(no data)	(no data)	0-38	(no data)
hl p.a.]											
Ethyl acetate	22	62	47	38	36	nd	1.3/no	nd-70	(no data)	0.8-164	(no data)
[g/hl p.a.]	2.2	02	т/	50	50	nu	limit	nu-70	(iio data)	0.0-104	(iio data)
Ethyl lactate	2.4	50	75	38	39	nd	-	(no data)	(no data)	0-66	(no data)
[g/hl p.a.]								()	()		()
Sum of	36	269	165	155	157	34	0.5/no	180-460	(no data)	(no data)	(no data)
higher							limit		. ,	. ,	
alcohols							(minimun	n			
[g/hl p.a.]							200)				

Table 2. Volatile composition of Nigerian surrogate alcohol in comparison to EU limits and data from the literature

nd: not detected (detection limit 0.5 g/hl p.a.)

¹recalculated from original data in wt-% or mg/l

²recalculated to g/hl p.a. under assumption of an alcoholic strength of 40% vol

³data reported for "butanol", no differentiation between isomers was made

39.9% previously reported for African ogogoro (Odunfa and Oyewole, 1998). Two samples had an alcohol content above 42% vol. The range is also consistent with the one given in a report about African traditional beverages from Tanzania (Mosha et al., 1996). In general, the alcoholic strength of the Nigerian spirits corresponds to the usual strength of European style spirits of around 40% vol (Lachenmeier and Musshoff, 2004). Surrogate alcohols from Russia and Eastern Europe were reported to contain higher alcoholic strengths than commercial spirits (Lang et al., 2006; McKee et al., 2005). This observation was not made in our Nigerian sample collection. Therefore, with respect to ethanol, we were not able to differentiate between the surrogate samples and commercial alcoholic beverages with similar strengths.

Volatile composition

In addition to ethanol, the samples contain a number of volatile compounds, which are

[mg/l]	1	2	3	4	5	6	EU Drinking water quality standards (EC, 1988)	WHO Guidelines for Drinking-water quality (WHO, 2006)
							,	
Al	nd	0.022	0.011	nd	0.063	nd	0.2	-
В	nd	nd	nd	0.61*	1.4*	0.051	1.0	0.5
р.	0.025				0.007	-		0.7
Ba	0.035 0.001	nd	nd	nd	4 0.004	nd	-	
Bi	0.001	nd	nd	nd	0.004 9	nd		
							-	-
Ca	3.7 0.002	0.94	2.3	0.84	3.8	2.5	-	-
Co	1	nd	nd	nd	nd	nd	-	-
Cr	nd 0.000	nd	nd	nd	9	nd	0.05	0.05
Cs	9	nd	nd	nd	nd	nd	-	-
Cu	0.11	3.6*	3.7*	2.1*	1.2	0.014	2.0	2
	0.002		0.003					
J	8	nd	9	nd	nd	nd	-	-
Κ	11	4.5	3.7	3.4	93	7.1	-	-
Mg	1	0.13	0.47	0.13	4.9	0.39	-	-
Mn	0.043	0.028	0.032	0.009	0.15*	nd	0.05	0.4
Na	54	25	5.4	2.5	3.9	17	-	-
Ni	nd	0.007	nd	nd	nd	nd	0.02	0.07
Р	0.074	0.17 0.001	0.036	0.057	1.8	0.16	-	-
Pb	nd	5	nd 0.003	nd	nd	nd	0.01	0.01
Rb	0.015	0.004	5	0.001	0.18	0.004	-	-
Si	nd	nd	0.22	nd	0.88	1	-	-
		0.004	0.007	0.001				
Sr	0.015	5	9	4	0.015	0.028	-	-
	0.001				0.008	0.001		
Ti	5	nd	nd	nd	5	4	-	-
						0.002		
W	nd	nd	nd	nd	nd	8	-	-
Zn	0.066	0.7	0.93	0.12	$0.085 \\ 0.002$	0.019	-	-
Zr	nd	nd	nd	nd	9	nd	-	-
Notes: "	'nd'' not c	letected; *	value abo	ve limit of	f EU or W	HO for dr	inking water (no limits	for spirits available)

Table 3. Inorganic composition of Nigerian surrogate alcohol in comparison to WHO and EU limits (results of ICP-MS semiquantitative analysis)

expected in products derived from alcoholic fermentation.

The methanol content was relatively low (i.e. lower than the EU limit of 50 g/hl p.a. for neutral alcohol). This fact shows that the products were not manufactured from fruit materials, which would lead to significantly higher methanol concentrations (usually above 100 g/hl p.a.). At this stage we can only speculate from which raw materials the spirits were manufactured, as no literature data for comparison are available.

Methanol is the substance most often associated with the toxicity of surrogate alcohol (Lachenmeier et al., 2007a). However, the low methanol concentrations in the Nigerian spirits are of no toxicological concern. The maximum tolerable concentration of methanol in alcoholic beverages is 2% vol, which equates to approx. 5000 g/hl p.a. (Paine and Dayan, 2001). This is above 150 times higher than the highest concentration of 31 g/hl p.a. found in the samples. Our results are in total agreement

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Sample	1	2	3	4	5	6	EU Drinking water quality standards (EC, 1988)	WHO Guidelines for Drinking-water quality (WHO, 2006)
Conductivity							2500	-
[µS/cm] Chloride	133	57 29.	_*	19	88	36	250	-
[mg/l] Nitrate	46.7	3	3.9	nd	3.9	nd	50	50
[mg/l]	29.1	nd	nd	nd	2.3	13.3		
Phosphate							-	-
[mg/l]	nd	nd	nd	nd	6.8	nd	250	
Sulfate [mg/l]	13.1	nd	nd	nd	8.3	nd	250	-

Table 4. Conductivity and anionic composition of Nigerian surrogate alcohol in comparison to WHO and EU limits

Notes: "nd" not detected (detection limits: chloride 2 mg/l, nitrate 5 mg/l, phosphate 10 mg/l, sulfate 5 mg/l); *not determined because the sample amount was too small

with the only study of the volatile composition of Nigerian ogogoro available in the literature to our knowledge: Odeyemi (1980) analyzed 7 samples of ogogoro and found that they did not contain any significant amounts of methanol and that there was clearly no risk of methanol poisoning from the ogogoro in their study.

Acetaldehyde is an undesirable substance in spirits because of its unpleasant flavour. It is also regarded as possibly being carcinogenic to humans (Group 2B) (IARC, 1999). During distillation acetaldehyde is enriched in the first fraction, which is generally discarded (Pieper et al., 1987). During production of spirits acetaldehyde may be formed not only as a product of alcoholic fermentation by Saccharomyces yeast, but also as a metabolite of microorganisms like lactic acid bacteria or acetic acid bacteria. Therefore, an increased amount of acetaldehyde usually indicates flaws in the fermentation process. Using German standard distillation stills most of the acetaldehyde can be separated. Nevertheless, a complete separation is not technically possible. An average acetaldehyde residue of between 12-18 g/hl p.a. (48-72 mg/l) can be found in German fruit spirits according to Pieper et al. (1987). The acetaldehyde content of the Nigerian spirits is in excellent agreement with the range found in German fruit spirits. The first distillation fractions appear to have been separated during production of the spirits. Another indication of this is the relatively low concentrations of ethyl acetate, which is also enriched in the first fractions.

Alcohols with more than two carbon atoms are commonly called 'higher' or 'fusel' alcohols (sometimes volatiles in alcoholic beverages besides ethanol are also called congeners). Most higher alcohols occur as by-products of yeast fermentation, and are important flavour compounds. The content of higher alcohols in alcoholic beverages is generally not seen as of toxicological relevance. For example, the Joint FAO/WHO Expert Committee on Food Additives included higher alcohols (1-propanol, 1butanol, isobutanol) in the functional class 'flavouring agent' and commented that there was no safety concern at current levels of intake when used as a flavouring agent (JECFA, 1997). For certain groups of spirits, the European Union even demands a minimum volatile substance content (i.e., the quantity of volatile substances other than ethanol and methanol, which are mainly higher alcohols). For example, fruit spirits must have a content of volatile substances of at least 200 g/hl p.a., whereas neutral alcohol should be almost entirely free of higher alcohols (max. 0.5 g/hl p.a. (European Council, 1989). The higher alcohols in our samples were generally lower than 200 g/ hl p.a. (one exception with 269 g/hl p.a.). The higher alcohols in our study were lower than those reported by Odeyemi (1980). It is not known whether this is the result of improved production techniques since the writing of the paper by Odeyemi, or if the differences purely derive from variations between the raw materials or yeast strains used. The concentrations of higher alcohols in our Nigerian samples were also lower than those reported in Russian samogon or legal fruit spirits (see Table 2 for comparison).

Non-volatile compounds and water quality

Because elements and ions are generally non-volatile, most of the inorganic content found in the spirits is derived from water used for dilution to drinking strength. Inorganic contamination may occur from use of the distillation equipment. For example, during the production of moonshine in the U.S., the leaching of lead from solder or other lead-containing materials in the radiators caused lead contamination of the moonshine (Lachenmeier et al., 2007a). In the Nigerian spirits, lead was only detected in one case in a very low lead level of 0.0015 mg/l, which is below the drinking water standard of the WHO and EU (0.01 mg/ 1) (European Council, 1988; WHO, 2006). Our samples therefore offer no explanation of the previous observation that excessive alcohol use may cause increased blood lead concentrations in alcohol users in Nigeria (Adeniyi and Anetor, 1999).

The drinking water standards were exceeded by one product for manganese (0.15 mg/l), by two products for boron (0.61 and 1.4 mg/l), and by three products for copper (2.1, 3.6 and 3.7 mg/l). The origin of manganese and boron is most likely the water. Our results verify the findings of Ukhun et al. (2005), who reported that the mineral contamination of Nigerian palm wine might have occurred during the bottling stage, most likely from the dilution water. In contrast, the copper concentrations may be possibly traced to the copper stills used for distillation as the major source. It is therefore not atypical to find copper levels of this magnitude in spirits, e.g. levels as high as 5.31 mg/ l of copper were measured in sherry brandies (Cameán et al., 2000) or levels up to 9.2 mg/ l (Bettin et al., 2002) or up to 14.3 mg/l (Nascimento et al., 1999) of copper in Brazilian sugar cane spirits. Our study therefore verifies the previous view that copper levels in Nigerian foods well compare to similar food items from other parts of the world (Onianwa et al., 2001).

For toxicity evaluation, it should be noted that the limits were derived for drinking water, which has a much higher rate of daily consumption than spirits. While some of the spirits under investigation slightly exceeded the drinking water limits, it cannot be concluded that such spirits are toxic or unsuitable for consumption. However, the Codex alimentarius general standard for contaminants and toxins in foods requires that contaminant levels shall be as low as reasonably achievable and that contamination be reduced by applying appropriate technology in food production, handling, storage, processing and packaging (Codex alimentarius, 1997). In this regard, we think that inorganic contaminants should be reduced in the spirits, especially in the drinking water, from which they are derived.

The samples were analyzed for inorganic anions, because of the nitrate problem that was previously described for Nigerian water supplies and alcoholic beverages (Bassir and Maduagwu, 1978; Ezeagu, 1995; Ezeonu et al., 1992). Nitrate may pose a public health problem because it may be a precursor in the formation of carcinogenic nitrosamines, which have been of some concern in the Nigerian diet (Maduagwu & Bassir, 1979). The nitrosamine contamination itself was previously found to be a negligible problem in Nigerian alcoholic beverages (Maduagwu & Uhegbu, 1986).

We have detected nitrate in three of the samples in concentrations up to 29.1 mg/l, which is below the drinking water limit, and much lower than levels up to 360 mg/l that were reported from contaminated Nigerian water supplies (Ezeonu et al., 1992). The conductivities of the samples were also relatively low, indicating an overall sufficient water quality or water treatment processes. Conclusions and health implications

The debate on the composition and possible harmful effects of home brews has been of concern and has been brought to the attention of the media in Africa. As an example, on Thursday Sept.1, 2005, the BBC program Africa Live invited their audience to comment on whether home brews have a place in modern Africa. In their introduction they stated that 'Local brews can provide much-needed money for poor families. But if not brewed properly, they can be dangerous and each year hundreds of people die after drinking these spirits'. We were thus surprised at the high quality of the beverages analyzed in this study. The samples contained concentrations of alcohol that were in agreement with those previously reported for ogogoro, but the concentrations of the other components (e.g., methanol, lead) were well below those associated with acute toxic effects. However, our findings must be interpreted with caution because the samples were obtained from a defined geographical area and thus may not be representative of the composition of home brews produced in other parts of Nigeria where different raw materials and possibly contaminated water may be used in the manufacturing process.

Although these findings are encouraging, the situation must be constantly monitored. These surrogate alcohol beverages are produced illegally and the production is uncontrolled. Therefore the composition of these beverages may change rapidly and result in harmful consequences.

There was one disturbing finding in this study. One sample of the home brew contained an unknown additive and was being sold as an 'antimalarial'. One of the authors (O.E.) who lives in Nigeria claims that this is a common practice. Malaria is endemic in Nigeria and use of these home brews as 'antimalarials' can have public health consequences because it can deter individuals from getting proper treatment for this debilitating condition. Further investigation of these additives is needed.

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