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Volatile compounds of maari, a fermented product from baobab (*Adansonia digitata* L.) seeds

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The volatile compounds associated with baobab seeds fermentation for Maari production were extracted and analysed by Likens-Nickerson simultaneous steam distillation-extraction method and gas chromatography-mass spectrometry (GC-MS), respectively. Furthermore, the titratable acidity, tannin content and proximate composition were evaluated. A total of 96 compounds were identified with esters, acids, alcohols and ketones being quantitatively the major groups. Fermentation led to an increase in the concentration of total volatile compounds from 121.6 in unfermented cooked seeds to 809.1 mg kg^{-1} in the fermented product. Drying resulted in a significant loss of up to 80.7% of the total volatiles.

Key words: Volatile compounds, maari, baobab, fermentation.

INTRODUCTION

Several fermented food condiments are commonly found in several African and Asian countries (Parkouda et al., 2009). In these countries, they are extensively used due to their pleasant taste and particular odour as well as their important nutritional qualities (Azokpota et al., 2008; Ouoba et al., 2005; Owens et al., 1997). Volatile compounds are one of the most valuable traits contributing to their quality and sensorial attributes (Beaumont, 2002). Maari is one of these fermented food condiments obtained by processing and spontaneous fermentation of seeds from the baobab tree (*Adansonia digitata* L.) in Burkina Faso. The process is laborious, energy- and time-consuming and procedures are based on traditional knowledge and experience of each processor. Contrary to similar fermented condiments produced from African locust beans (Soumbala, afitin, iru, sonru and netetu), the

baobab cooked seeds were not dehulled before the fermentation; this can lead to a difference in the chemical content and the profile of volatile compounds. Maari is especially used as flavouring agent for sauces, soups and other dishes in some African countries (Chadare et al., 2008; Parkouda et al., 2010). Traditional maari is characterized by a specific strong odour which is the main criterion used by consumers to appreciate the quality of the condiment. Similar products like afitin, chungkuk-jang, iru, natto, sonru, soumbala and thua-nao have been extensively studied and a diversity of volatile compounds reported (Azokpota et al., 2008; Leejeerajumnean et al., 2001; Ouoba et al., 2005; Tanaka et al., 1998). The flavour of these condiments has mainly been attributed to various volatile compounds produced through the metabolic activities of micro-organisms during fermentation or the processing conditions (Azokpota et al., 2008; Leejeerajumnean et al., 2001; Ouoba et al., 2005). Differences in the traditional processes for fermented condiments occur among ethnic

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tribes and these differences presumably influence the quality of the final products. The identification of volatile compounds is one of the steps which could give information for a future selection of starter culture to be used in controlled fermentation (Azokpota et al., 2010). In afitin, iru and sonru, compounds belonging to pyrazines, aldehydes, ketones, esters, alcohols, acids, alkanes, alkenes, benzenes, phenols, sulphurs and furans groups were identified (Azokpota et al., 2008). In addition to these compounds, Ouoba et al. (2005) found amines and pyridines groups in soumbala. However, volatile compounds that characterize maari have not yet been reported. The aim of the present study was to investigate the volatile compounds associated with spontaneous fermentation of baobab seeds for maari production using Likens-Nickerson simultaneous distillation-extraction method and gas chromatography mass spectrometry (GC-MS).

MATERIALS AND METHODS

Maari processing and sampling

Maari samples were obtained by spontaneous fermentation of baobab seeds by three producers (V, C and B) from Pousghuin (a village in Zorgho, Burkina Faso) according to their own procedure. Briefly, maari production was done as follows: The baobab seeds were cleaned and boiled for about 36 h. After the 24 h of boiling, an ash lye solution was added as softening agent. After the boiling period, the seeds were drained and transferred into a basket and left to ferment spontaneously (first fermentation) for 72 h at room temperature (30 to 35°C). The fermenting mash was pounded and moulded with further addition of the alkaline ash lye solution. It was left to undergo a second spontaneous fermentation for about 24 h at room temperature before drying, including an initial steam cooking step. The final product obtained was characterized by dark brownish colour, stickiness and strong smell. Maari is sometime slightly roasted to give a specific trait to the product. For each of the three producers, duplicate unfermented boiled seeds, fermenting mash just before steam cooking and the final dried maari were collected from the producers and stored at -20°C before analysis. Additional commercial dried maari ready for consumption was also collected at Toulfé (a village in Burkina Faso) for comparison. The analyses were performed in triplicate.

Proximate analysis

Moisture, protein, lipid and ash analyses were determined according to AOAC official methods (AOAC, 2005). The tannins content of the samples were estimated by the vanillin-HCl colorimetric method as described by Addy et al. (1995). The tannins were extracted with methanol (Merck, Darmstadt, Germany) and made to react with the vanillin reagent (Merck, Darmstadt, Germany), to produce a colour reaction, which was measured spectrophotometrically at 500 nm. The calibration curve was established with (+)-catechin (Merck, Darmstadt, Germany). For titratable acidity (TA), 5 g of sample was mixed with 50 ml of distilled water and mixed in a stomacher (Stomacher 400 Lab Blender, London, England) at normal speed for 4 min. After filtration through a Whatman paper filter, the TA was evaluated by titrating the filtrates with 0.1 N sodium hydroxide (Merck, Darmstadt, Germany) using

phenolphthalein as the indicator (Jideani and Okeke, 1991).

Extraction and identification of the volatile compounds

Extraction of volatile compounds

The simultaneous distillation and extraction method described by Nickerson and Likens (1966) was used for the investigation of the volatile compounds of the different types of maari. The volatile compounds of the samples were extracted using a microscale steam distillation low density solvent extraction device (micro-SDE; Chrompack, Middelburg, the Netherlands) as described by Annan et al. (2003) and modified as follows: a known quantity of pounded samples (according to their moisture content) was mixed in 400 ml distilled water to obtain 2.5% slurries (on dry weight basis) of samples (w/v). A 1 ml internal standard solution (2-methyl-1-propanol) was added to the sample slurry in a 1000 ml Erlenmeyer flask. About 6 ml of a mixture of pentane and diethyl ether (1:1) was placed in a 9 ml pear-shaped solvent flask. Both flasks were connected to the distillation apparatus and the solutions were brought to boil. Extraction of volatile compounds was carried out for 30 min, from the beginning of condensation of vapours on the walls of the condenser. The organic solvent phase was collected and stored at -20°C to freeze out any water present. The solvent extract was poured off, dried over 2 g of anhydrous Na_2SO_4 and concentrated to 100 mg by gently blowing N_2 gas over the surface. The concentrated extract was analyzed for volatile compounds using gas chromatography and mass spectrometry (GC-MS). Extractions were performed in triplicate.

Separation and identification of the volatile compounds by GC-MS

Separation and identification of volatile compounds in the concentrated extract was performed on a Varian CP 3900 GC/MS equipped with Varian CP-8400 Autosampler (GC-MS; Varian, NA, USA). Two microlitres of extract were injected (split ratio, 1:20) into Varian factor four capillary column (VF-5ms) (30 m x 0.25 μm x 0.39 mm film thickness) using the temperature program: 10 min at 40°C, raised at 6°C min^{-1} to 240°C and then, maintained for 30 min at 240°C. The carrier gas was helium with a constant flow rate of 1 ml min^{-1}.

The MS detector conditions were as follows; transfer line temperature, 250°C; manifold temperature, 80°C; ion trap temperature, 20°C; ionisation mode, EI auto; mass range, 25 to 550 m/z; multiplier delay, 1.77 min.

Identification of volatile compounds was determined in the total ion mode scanning a mass to charge ratio (m/z) range between 25 and 550. Further identification was obtained by probability-based matching with mass spectra in the NIST 05 mass spectral library (Varian). Only compounds showing high quality index (degree of agreement between mass spectrum of sample and mass spectrum in database ≥ 90) were retained. Concentrations of volatile compounds were estimated by comparing the relative peak areas of the compounds with that of the 2-methyl-1-propanol internal standard and reported in mg kg^{-1} based on the concentration of the internal standard.

Statistical analysis

Differences between mean values were determined by analysis of variance and Student-Newman-Keuls test using SAS statistical software package (SAS, release, 8.1, Cary, N.C., USA).

RESULTS

As seen from Table 1, during fermentation, protein content decreased from 156 ± 4.1 g kg^{-1} to values ranging from 147 ± 0.7 to 134 ± 0.5 g kg^{-1} dry weight basis, while lipid content increased from 122 ± 5.3 g kg^{-1} to values ranging from 151 ± 3.8 to 181 ± 1.5 g kg^{-1}. Ash content increased from 45 ± 0.4 up to 88 ± 3.6 g kg^{-1}. The titratable acidity of unfermented baobab seeds had a value of 0.17% OAE and increased to 1.87% in the fermented product. The tannins content decreased from 0.29 mg g^{-1} CE to values between 0.25 and 0.09 mg g^{-1} after fermentation. Changes resulting from the fermentation were statistically significant ($P < 0.05$).

The results in Table 2 show that, a variety of volatile compounds characterized the studied samples and a total of 96 volatile compounds were found. They belonged to 10 groups of compounds including acids (6), alcohols (13), aldehydes (6), alkanes (2), alkenes (2), esters (23), ketones (22), pyrazines (7), sulphur compounds (4) and others (11). Esters, ketones, alcohols groups constituted the groups with the largest number of volatile compounds.

No volatile compounds belonging to the aldehydes, alkenes and pyrazines group were found in the unfermented cooked seeds (UCS). Fermentation led to an increase in the concentration of total volatile compounds from 121.6 mg kg^{-1} in an unfermented cooked seeds (UCS) up to 809.1 mg kg^{-1} in the fermented product (ZV1). In the fermented samples, the total volatile compounds were 809.1, 582.9 and 636.8 mg kg^{-1}, respectively, for ZV1, ZC1 and ZB1; after the drying process, they were 291.3, 204.03 and 123 mg kg^{-1} for ZV1, ZC1 and ZB1, respectively. Drying process resulted in an important loss up to 80.7% of the total volatiles including principally esters, alcohols and acids groups. The amount of the volatile compounds in the dried commercials maari sample (DTA) was 352.9 mg kg^{-1}.

Qualitatively, only few volatile compounds including 2-nonadecanone, γ-dodecalactone, 2-decanone, 3-ethyl-2-pentanone, 14-methyl pentadecanoate, di-tert-Butyl dicarbonate, ethyl acetate, Z,Z,Z-4,6,9-nonadecatriene, nonadecane, benzeneacetaldehyde and 2,4-dimethyl-3-pentanol were common in all dried fermented samples from the three producers, showing a specificity of each sample. Table 3 shows that, the relative amounts of the compound groups varied widely among samples and ranged from 0.0 to 65.4%. The major compounds group found in unfermented cooked seeds was sulphur compounds (26% of its total amount of volatiles). No aldehydes, alkynes, furans, phenols and pyrazines compounds were found in the unfermented cooked seeds. In the fermented products, the major compounds found generally were alcohols, aldehydes, alkanes, esters and ketones groups. The sample ZB1 showed the highest relative amount of esters (65.4%), ZV1 for ketones (37.3%) and ZC1 for alcohols (26%), which were the common components groups among all the samples. The commercial samples DTA stands out significantly as the sample richest in the content in pyrazines group (20%).

DISCUSSION

Production of maari resulted in a decrease of carbohydrates. Decrease in carbohydrates has been reported in previous studies on similar products like bikalga and daddawa (Parkouda et al., 2008; Ibrahim and Antai, 1986). The decrease is likely to be explained by cooking and loss of carbohydrate in the cooking water and by the fermentation where carbohydrates are metabolised by the microorganisms responsible for fermentation (Parkouda et al., 2008). The formation of some volatile aroma compounds belonging to ketones and aldehydes groups which are generally formed via Maillard reactions between saccharides and peptides may also play a role (Ledauphin et al., 2003). The increase of the titratable acidity observed is likely due to the accumulation of acid from the hydrolytic activities of the amylolytic enzymes (Schaffner and Beuchat, 1986) as well as the role of microbial metabolism such as lactic acid bacteria and *Bacillus* spp. during fermentation. The observed decrease in tannins during fermentation is in line with previous studies on baobab seeds (Addy et al., 1995; Nnam and Obiakor, 2003). Hydrolysis of the polyphenolic compounds to simpler substances by the enzyme polyphenol oxidase or the breakdown of the tannin complexes for example, tannin-protein, tannic acid-starch and tannin-iron complexes to release free nutrients could explain this decrease (Obizoba and Atti, 1991). Chemical content, including titratable acidity and tannins is expected to contribute to the sensorial quality and volatile compounds profiles of the different samples. For instance, free fatty acids are known to contribute positively to the production of characteristic flavours in food but high levels of fatty acids may easily cause rancidity (Nawar, 1985).

In maari, as other fermented condiments, volatile aroma compounds are important for quality and sensorial attributes. A number of volatile compounds are present in the unfermented baobab cooked seeds; others are produced during fermentation. The volatile compounds found in the unfermented cooked seeds can be explained by a complex sequence of chemical reactions, for example, strecker degradation, taking place as a function of moisture, cooking temperature and duration (Rodríguez-Bernaldo De Quirós et al., 2000). Esters group found in the unfermented cooked seeds were also reported previously in unfermented cooked Africa locust bean (Azokpota et al., 2008; Ouoba et al., 2005). In contrast, no ester was reported in unfermented cooked Africa locust bean during controlled production (Azokpota et al., 2010). The latter result can be explained by the severe heat treatments applied to the locust beans, leading to complete loss of esters due to thermal degradation

Table 1. Chemical composition[†] of Unfermented and Fermented baobab seeds*.

Sample	Compound						
	Moisture (g kg^{-1})	Protein (g kg^{-1})	Lipid (g kg^{-1})	Ash (g kg^{-1})	Carbohydrate (g kg^{-1})	Titratable acidity (% OAE)	Tannin (mg g^{-1} CE)
Seeds	59 ± 0.5^d	156 ± 4.1^a	122 ± 5.3^c	45 ± 0.4^d	619	0.17 ± 0.03^d	0.29 ± 0.09^a
ZB2	134 ± 0.5^a	147 ± 0.7^b	181 ± 1.5^a	73 ± 3.1^b	465	1.47 ± 0.07^b	0.10 ± 0.06^b
ZC2	103 ± 0.6^c	142 ± 4.1^c	177 ± 3^a	68 ± 1.3^c	511	1.87 ± 0.08^a	0.25 ± 0.08^a
ZV2	131 ± 0.2^b	134 ± 0.5^d	151 ± 3.8^b	88 ± 3.6^a	491	0.77 ± 0.01^c	0.09 ± 0.01^b

Results are expressed on dry weight basis. *Data are expressed as mean ± standard deviation (n = 3). Means values in a column with the same letter are not significantly different at 95% confidence. ZC2, ZV2 and ZB2, Dried maari samples ready for consumption collected respectively from producer C, V and B; CE, catechin equivalents; OAE, oleic acid equivalent.

Table 2. Volatile compounds of cooked unfermented baobab seeds (UCS) and various samples of maari.

RT	Volatile compound	Mean concentration (mg kg^{-1} of product dry weight basis)							
		UCS	ZV 1	ZV2	ZC1	ZC 2	ZB 1	ZB 2	DTA
Acid (6)									
12.14	2,2-dimethyl propanoic acid	1.6^b	-	-	-	-	7.5^a	-	-
14.67	2-methyl-Propanoic acid	-	-	-	-	13^a	0.7^b	-	-
19.99	2-(aminooxy) pentanoic acid	1.3^b	-	-	-	-	4^a	-	-
22.7	Benzoic acid	-	-	-	-	-	1.0^a	0.7^a	-
38.78	Palmitic acid	2.9^f	-	8.1^d	30.6^a	5.3^e	18.5^b	-	14.7^c
41.58	Oleic acid	-	44.3^a	2.7^e	6.5^d	-	14.4^b	0.9^f	8.7^c
	Total acids	5.83	44.34	10.78	37	18.35	46.18	1.6	23.39
Alcohol (13)									
13.88	1-isopropoxy-2-methyl-2-Propanol	1^d	5.5^a	-	4.4^b	-	2.5^c	-	-
14.91	3,3-Dimethyl-2-pentanol	0.2^b	-	-	-	-	6.8^a	6.4^a	-
18	2-methyl-3-hexanol	0.8^d	9.2^a	4.5^b	-	1.5^c	-	-	1.1^{c,d}
22.2	2,4-dimethyl-3-pentanol	3.6^f	86^a	19^c	50.3^b	14.3^d	4^f	4.3^f	11.3^e
22.22	2,4,4-trimethyl-1-pentanol	0.5^d	75^a	11.5^c	-	19.7^b	-	-	-
22.37	1,5-hexadien-3-ol	12^c	-	-	61.2^a	-	48.1^b	13.7^c	-
22.43	5-methyl-4-octanol	-	12.5^a	-	3.9^b	-	-	-	-
23.53	2-dodecanol	0.2^b	-	-	-	-	0.6^a	-	-
25.07	2-pentadecyn-1-ol	-	-	-	31.6^a	1.1^b	-	-	-
26.42	2,5-dimethyl-1,5-hexadiene-3,4-diol	-	-	-	-	-	9.3^a	3.5^b	-
26.43	2-(hydroxymethyl)-2-methyl-1,3-propanediol	1.8^a	-	-	-	-	1.7^a	-	-
30.93	1-hexadecanol	-	-	-	-	-	1.2^a	1.0^b	-

Table 2 cont.

45.11	2-hexyl-1-octanol	1.0[c]	7.2[a]	-	-	-	1.5[b]	0.8[c]	-
	Total alcohols	21.04	195.19	34.88	151.28	36.53	75.67	29.62	12.45
Aldehyde (6)									
6.69	3-Bromopropionaldehyde Ethylene acetal	-	-	-	-	-	30.6[b]	15.6[c]	44.1[a]
13.26	Heptanal	-	-	-	4.8[a]	-	-	-	1.3[b]
17.58	Octanal	-	-	1.6[d]	21.3[a]	-	3.7[c]	0.2[e]	4.3[b]
19.01	Benzeneacetaldehyde	-	-	22.6[a]	-	8.3[c]	2.8[d]	1.8[e]	9.7[b]
26.41	(E,E)-2,4-nonadienal	-	-	2.9[b]	56.5[a]	3.6[b]	-	-	-
26.42	2,4-Decadienal	-	-	-	15.4[a]	-	1.2[c]	-	2.9[b]
	Total aldehydes	0	0	27.1	97.95	11.86	38.3	17.61	62.35
Alkane (2)									
45.52	Nonadecane	-	-	1.1[c]	16.1[a]	1.4[b]	1[c,d]	1[d]	-
47.68	Tetratetracontane	0.9[d]	-	-	8.3[a]	0.8[e]	1.7[b]	0.6[f]	1.3[c]
	Total alkanes	0.9	0	1.11	24.35	2.22	2.69	1.51	1.3
Alkenes(2)									
20.85	Z-1,9-hexadecadiene	-	-	-	5.3[a]	4.2[b]	-	1.8[c]	5.1[a]
33.47	Z,Z,Z-4,6,9-Nonadecatriene	-	-	9.7[a]	4.8[b]	0.9[d]	-	1.9[c]	1.5[c,d]
	Total alkenes	0	0	9.7	10.08	5.06	0	3.7	6.55
Ester (23)									
7.7	Methoxyacetic acid, pentyl ester	1.2[b]	-	-	-	-	-	-	5.2[a]
13.96	Isobutyl isobutyrate	2.1[c]	10.3[a]	-	9.4[b]	2.4	9.2[a,b]	2.6[c]	2.1[c]
14.29	2-butanol, 2-nitrosoacetate	1.3[a]	-	-	-	0.8[b]	-	-	-
14.74	Ethyl acetate	2.1[c]	-	2.6[c]	10.3[a]	3.5[b]	3.4[b]	3.4[b]	2.4[c]
18.79	Vinyl butyrate	5.9[b]	-	-	11.8[a]	2.2[d]	2.7[c]	2.3[c]	2.1[c,d]
24.87	2-phenylethyl acetate	-	-	1.1[c]	15.2[a]	1.3[b]	-	-	-
24.98	di-tert-butyl dicarbonate	5[c]	37.8[a]	5[c]	28[b]	1.5[d]	5.4[c]	1[e]	1.1[d,e]
38.11	14-methyl pentadecanoate	-	-	4.7[c]	14.3[b]	17.1[a]	-	2.2[d]	-
38.12	Methyl hexadecanoate	0.3[d]	4.7[c]	-	-	-	12[b]	-	13.3[a]
38.89	L-(+)-ascorbic acid 2,6-dihexadecanoate	-	116.9[a]	-	-	-	64.1[b]	-	-
39.22	Ethyl hexadecanoate	0.9[f]	26[b]	14.6[d]	9.7[d]	7.9[e]	109.5[a]	-	15.3[c]
40.36	Methyl 7,10-octadecadienoate	-	-	-	-	-	4[a]	-	1.3[b]
40.72	Propyl hexadecanoate	-	-	1.5[b]	-	-	7.8[a]	-	-
40.78	Methyl 9,12-octadecadienoate	-	7[c]	1.9[f]	5.2[d]	2.5[e]	18.1[a]	-	7.7[b]
40.9	Methyl (Z)-9-octadecenoate	-	10.6[b]	3[f]	6.9[d]	3.6[e]	20.5[a]	-	8.3[c]

Table 2. cont.

41.36	9,12-octadecadienoate	-	-	-	-	-	52.5	-	-
41.83	Ethyl (Z,Z) 9,12-octadecadienoate	-	-	5.3[c]	-	2.3[d]	33.1[a]	-	6.4[b]
41.84	Ethyl linoleate	0.5[b]	17.8[a]	-	-	-	0.2[c]	-	-
41.87	Ethyl (E)-9-octadecenoate	-	-	-	6.7[b]	-	-	-	11.1[a]
41.9	Ethyl oleate	0.6[f]	8[c]	8.2[b]	4.6[d]	3[e]	68.4[a]	-	8[b,c]
42.21	Butyl hexadecanoate	-	7.8[a]	-	-	-	0.7[b]	-	-
44.06	Isopropyl linoleate	-	8.9[a]	-	-	-	2.5[b]	-	-
44.39	Decyl oleate	-	11.8[a]	-	-	-	2.3[b]	-	-
	Total esters	20.47	267.46	47.79	121.98	48.13	416.31	11.51	84.19
	Ketone (22)								
8.23	3,4-dimethyl-2-pentanone	9.1[b]	-	-	-	-	10.5[b]	10.3[b]	15.8[a]
8.24	3-methyl-2,4-pentanedione	-	-	16.9[a]	-	15.3[a]	-	-	-
8.96	3-ethyl-2-pentanone	3[d]	-	4.7[b]	18[a]	4.1[c]	1[e]	0.9[e]	4.2[b,c]
9.77	4-methyl-2-hexanone	0.4[e]	-	4.2[b]	26.1[a]	3.5[c]	2[d]	-	3.5[c]
14.31	3-methyl-2-hexanone	2.2[b]	5.3[a]	-	-	1.2[c]	2.1[b]	-	-
14.81	3-hydroxy-2-butanone	2.8[a]	-	-	-	-	-	2.6[b]	3[a]
15.94	2-chloro-3-methyl-1-phenyl-1-butanone	-	26.7[a]	-	-	7.8[b]	-	-	-
15.95	2-chloro-acetophenone	-	-	17.9[b]	-	0.6[c]	-	16.5[b]	21.1[a]
16.01	2,2-dihydroxy-1-phenyl-ethanone	-	-	-	-	1.7[b]	-	-	7.4[a]
18.78	3-Hydroxybutanone	-	74.1[a]	-	-	-	-	-	12.3[b]
20.48	2,5-dimethyl-4-hydroxy-3-hexanone	1.3[d]	19[a]	-	8.2[b]	4[c]	1.2[d]	-	-
23.24	2-decanone	-	27.9[a]	5.5[c]	14.6[b]	1.9[e]	2.6[e]	1[f]	4.1[d]
25.46	4,4,6-trimethyl-2-Cyclohexen-1-one	-	-	-	-	0.8[b]	-	-	3.4[a]
25.75	2-undecanone	-	-	3.3[a]	-	-	-	2.7[b]	-
26.88	3,5-dimethyl-2-octanone	-	78.9[a]	16.5[b]	9.4[c]	1[e]	1.5[d]	-	-
26.89	3-methyl-2-heptanone	-	-	-	-	2.4[a]	-	0.9[b]	-
28.05	2-dodecanone	-	16.9[a]	-	2.6[b]	-	0.6[c]	-	-
29.12	1-cyclododecyl-ethanone	-	14.9[a]	-	-	-	0.4[c]	1[b]	-
29.57	2,5-cyclohexadiene-1,4-dione	1.3[e]	21.8[a]	2.1[d]	11.5[b]	-	7.3[c]	0.9[f]	-
30.21	2-tridecanone	-	-	6.7[a]	-	-	1.7[b]	1.4[b]	-
33.91	Gamma. dodecalactone	-	16.7[a]	8.3[b]	-	1.6[c]	0.8[d]	0.6[d]	-
34.16	2-nonadecanone	-	-	5.6[b]	11.1[a]	1.2[d]	1[d]	0.9[d]	4.1[c]
	Total ketones	20.12	302.1	91.55	101.49	46.91	32.65	39.67	78.91
	Pyrazine (7)								
17.65	Trimethyl-pyrazine	-	-	-	-	-	-	-	2.4

Table 2 cont.

RT	Compound	UCS	ZV1	ZV2	ZC1	ZC2	ZB1	ZB2	DTA
19.38	1-(2-tetrahydrofurylmethyl) pyrazine	-	-	-	-	-	1.7	-	-
20.32	Tetramethyl-pyrazine	-	-	-	-	-	-	-	56.9
21.79	2-isobutyl-3-methylpyrazine	-	-	-	-	-	0.4	-	-
22.32	2,3,5-trimethyl-6-ethylpyrazine	-	-	-	-	-	-	-	9.9
25.36	2-(2-methylpropyl)-3,5,6-trimethylpyrazine	-	-	-	-	-	-	-	1.4
27.59	2,6-Bis(2-methylpropyl)pyrazine	-	-	-	-	-	2.2[a]	2[a]	-
	Total pyrazines	0	0	0	0	0	4.27	1.98	70.61
Sulphur compounds (4)									
2.66	Thioacetic acid	29.3[b]	-	52.3[a]	-	-	-	-	-
4.52	Disulfide, dimethyl	-	-	-	-	3.6[b]	4.1[a]	-	-
12.93	Diacetyl sulphide	0.8[b]	-	-	-	-	4.3[a]	0.5[c]	-
16.08	Dimethyl trisulfide	1.5[d]	-	-	7.4[b]	7.8[a]	3.1[c]	3.9[c]	1.7[d]
	Total sulphur compounds	31.63	0	52.28	7.44	11.48	11.56	4.44	1.71
Others (11)									
4.02	Tetrahydro-thiazole	20.3[a]	-	-	-	-	-	9.4[b]	-
11.79	d-Threo-O-ethylthreonine	1.1[b]	-	-	5.5[a]	-	-	0.8[b]	1.6[b]
16.92	Phenol	-	-	7.6[b]	-	9.3[a]	-	-	-
17	2-pentyl-furan	-	-	-	4.5[a]	-	-	-	-
17.13	O-(3-methylbutyl)-hydroxylamine	-	-	5.5[b]	-	-	1.2[b]	-	1.4[a]
18.19	1-undecyne	-	-	-	21.3[a]	5.1[b]	1.2[a]	-	-
25.91	Indole	-	-	1.8[b]	-	9.1[a]	0.1[c]	-	1.5[c]
26.25	2-methoxy-4-vinylphenol	-	-	1.2[b]	-	-	1.2[a]	-	1.5[a]
35.73	Benzamide	-	-	-	-	-	1.9[a]	1.2[a,b]	1.6[a,b]
35.93	O-decyl-hydroxylamine	0.2[b]	-	-	-	-	-	-	1.5[a]
37.88	7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-Diene-2,8-dione	-	-	-	-	-	3.6[a]	-	2.3[a]
	Total others	21.64	0	16.14	31.32	23.49	9.15	11.35	11.41
Total all compounds (96)		121.63	809.09	291.33	582.89	204.03	636.78	122.99	352.87

Only compounds showing high quality index were retained. Values are means of triplicate determinations. Means with the same letters in the same compound in a row are not significantly different (P < 0.05). –Compound not detected. UCS, Unfermented cooked beans; ZV1 and ZV2, maari samples from the producer V, collected respectively at the end of the fermentation (before the drying process) and after drying process; ZC1 and ZC2, maari samples from the producer C, collected respectively at the end of the fermentation (before the drying process) and after drying process; ZB1 and ZB2, maari samples from the producer B, collected respectively at the end of the fermentation (before the drying process) and after drying process; DTA, commercial sample collected at Toulfé in Burkina Faso; RT, retention time.

Table 3. Relative amounts of volatile compound groups identified in baobab unfermented cooked seeds and maari samples.

Aroma compound group	Relative amount of the compound groups (%)[a]							
	UCS[b]	ZV1	ZV2	ZC1	ZC2	ZB1	ZB2	DTA
Acids	4.8	5.5	3.7	6.3	9.0	7.3	1.3	6.6
Alcohols	17.3	24.1	12.0	26.0	17.9	11.9	24.1	3.5
Aldehydes	0.0	0.0	9.3	16.8	5.8	6.0	14.3	17.7
Alkanes	0.7	0.0	0.4	4.2	1.1	0.4	1.2	0.4
Alkenes	0.0	0.0	3.3	1.7	2.5	0.0	3.0	1.9
Esters	16.8	33.1	16.4	20.9	23.6	65.4	9.4	23.9
Ketones	16.5	37.3	31.4	17.4	23.0	5.1	32.3	22.4
Pyrazines	0.0	0.0	0.0	0.0	0.0	0.7	1.6	20.0
Sulfur Compounds	26.0	0.0	17.9	1.3	5.6	1.8	3.6	0.5
Others	17.8	0.0	5.5	5.4	11.5	1.4	9.2	3.2

[a] % Concentration of volatile compounds relative to the total concentration of volatile compounds identified; [b] unfermented cooked baobab seeds– group not detected; ZV1 and ZV2, maari samples from the producer V, collected respectively at the end of the fermentation (before the drying process) and after drying process; ZC1 and ZC2, maari samples from the producer C, collected respectively at the end of the fermentation (before the drying process) and after drying process; ZB1 and ZB2, maari samples from the producer B, collected respectively at the end of the fermentation (before the drying process) and after drying process; DTA, commercial sample collected at Toulfé in Burkina Faso.

(Rodríguez-Bernaldo De Quirós et al., 2000).

This study showed that, the fermentation of the baobab seeds for maari production led to an increase of volatile compounds. Increase of volatile compounds in other fermented condiments during fermentation was also reported in previous studies (Azokpota et al., 2008; Ouoba et al., 2005; Owens et al., 1997). The formation of volatile compounds during fermentation observed is obviously due to the microorganisms involved in fermentation as well as the processing factors such as boiling or roasting (Azokpota et al., 2010; Dakwa et al., 2005; Ouoba et al., 2005; Yuliana and Garcia, 2009). Indeed, difference between the volatile compounds profiles of soumbala samples was reported to rely on the variable ability of the species of microorganism to degrade the proteins, lipids and carbohydrates of African locust beans (Ouoba et al., 2005). Comparing volatile compounds produced during spontaneous and controlled fermentation of afitin, iru and sonru, a very pronounced increase of the concentration of total volatile compounds was reported during the use of *Bacillus subtilis* as starter culture (Azokpota et al., 2010). This increase was explained by the use of pure culture (Azokpota et al., 2010; Leejeerajumnean et al., 2001). Investigating on processing factors, Dakwa et al. (2005) found pre-treatment of soybeans by either boiling or roasting before fermentation to generate different volatile compounds profiles of soy-dawadawa.

The amount of the total volatile compounds decreased during the drying process resulting in a loss of up to 80.7% of the total aroma volatile compounds. A previous study on *Bacillus* fermented soybeans also reported a loss of aroma compounds during drying (Leejeerajumnean et al., 2001). This loss is attributable to most of the compounds simply evaporating during the open-air drying process. On the other hand, other volatile components like 2-undecanone, 2-chloro-acetophenone and 3-methyl-2-heptanone appeared in the dried maari and a few volatile compounds like dimethyl trisulfide were higher in the dried maari than in the fermented non-dried maari. These changes could probably be related to variable factors such as enzymatic activities, Maillard reaction, strecker degradation or microbial metabolism that could continue to occur during the drying process.

Overall, the volatile compounds reported in this study are highly variable and confirmed the non-standard production practices among producers. The present results support earlier studies that show the diversity of aroma volatile compounds in fermented food condiments such as Beninese afitin, iru and sonru, Burkinabe soumbala, Ghanaian soy-dawadawa, Japanese natto, Korean chungkuk-jang and Thai thua-nao (Azokpota et al., 2010; Azokpota et al., 2008; Dakwa et al., 2005; Leejeerajumnean et al., 2001; Ouoba et al., 2005; Tanaka et al., 1998). For soumbala, Ouoba et al. (2005) revealed the presence of pyrazines, aldehydes, ketones, esters, alcohols, acids, alkanes, alkenes, benzenes, phenols, sulphurs, furans pyridines and amines. Amines and pyridines were not found in afitin, iru and sonru (Azokpota et al., 2008). In addition to the chemical groups found in soumbala, (excluding pyridines) in this study, the presence of alkynes compounds was reported. In natto and thua-nao, ketones, acids and pyrazines were reported to be the major volatile compounds (Owens et al., 1997). Ester, mainly formed by esterification of carboxylic acids and alcohols was reported to determine the characteristic pleasant aromatic notes (Klesk and Qian, 2003; Rodríguez-Bernaldo De Quirós et al., 2000).

According to this study, maari shows a low level of pyrazines contrary to what has been reported for the

African locust bean fermented condiments such as afitin, iru, sonru and soumbala (Azokpota et al., 2008; Ouoba et al., 2005). Similar to our results, low presence of pyrazines was also recorded in soy-dawadawa obtained by boiled soybeans compared with roasted soybeans (Dakwa et al., 2005). The formation of pyrazines is generally associated with heating (Owens et al., 1997). Shu (1998) revealed that, pyrazines are characterized by their extremely high volatility and reactivity. Due to the physical proprieties of baobab seeds, the seeds are intensively cooked for about 36 h prior to the fermentation; this may be explained as the difference observed in the pyrazines content in the present study. The presence of arginine was also reported to decrease the yield of the pyrazines production (Hwang et al., 1995). In others studies, arginine content was recorded to be higher in baobab seeds (2.21 mg g^{-1}) than in African locust bean (0 mg g^{-1}), (Konlani et al., 1999; Glew et al., 1997) which could also explain the low content of pyrazines in fermented baobab seeds.

Diversity of the volatile components from each typical sample was observed. This difference may be explained by the specificity of each typical product giving specific compounds which are presumably more critical for the sensory characteristics as perceived (and probably expected) by consumers in tasting the product. In previous studies, the use of pure culture of micro-organisms led to uniform final fermented product preferred by a panel of consumers (Ouoba et al., 2005; Azokpota et al., 2010). This study is one of the steps which could give information for a future selection of starter culture to be used in controlled fermentation.

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