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Volatile flavour compounds of cooked acha (*Digitaria exilis* Stapf)

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Abstract

Volatile compounds obtained from cooked acha using a Tenax trap isolation method were identified on a GC–MS. Twenty-three compounds were identified and quantified. These compounds included aldehydes, hetero-cyclics, alcohols, hydrocarbons, an ester, a terpene and two benzene compounds. Major volatiles included ethylbenzoate, 2-pentylfuran, 2,5-dimethylpyrazine, trisiloxane, 2,6-dimethylpyrazine and 1,4-cyclohexadiene. Volatiles with smaller peaks comprised 4-vinylguaiacol, 2-acetylpyrroline, 2-methylpyrazine, toluene, pentanal, nonanal and 3-cyclohexen-1-ol. Although, not conclusive, GC-sniffing results indicated that the compounds with high probability of contributing to the aroma of cooked acha included pentanal, hexanal, hexanol, nonanal, benzaldehyde, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-acetylpyrroline and 2-pentylfuran. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Digitaria exilis (Stapf) is a cereal indigenous to the Sahel region in Africa (Annegers, 1973). Its common name is acha, fonio, or hungry rice. It belongs to the grasses family, Poaceae, and is grown as a rain-fed crop under marginal conditions and with low inputs, in areas which produce a more dependable harvest than other major crops (Rooney, Kirleis, & Murty, 1986). Acha is a staple cereal in the drier parts of tropical Africa where it is the sixth most important cereal after rice, wheat, maize, sorghum and pearl millet (Haq & Ogbe, 1995). It is considered to be the oldest West African cereal with cultivation dating back to 5000 BC (Purseglove, 1985).

Surprisingly, it has received little international attention. Acha is nutritious and its grains are rich in methionine (De Lumen, Thompson, & Odegard, 1993), an amino-acid vital to human health and deficient in many major cereals. The crop is used in a variety of ways in Africa. The small grains have an attractive flavour and are made into porridge and couscous, or are ground and mixed with other flours to make breads (Haq & Ogbe, 1995). Acha is an important food crop of tribal people of northern Nigeria where the ethnic groups may consume it three times a day in various ways (Jideani, 1990).

The properties of acha have received some attention (De Lumen et al., 1993; Jideani, Owusu, & Muller, 1994; Lasekan, 1996) due to some of its outstanding nutritional qualities. The proteins in acha have been characterized by electrophoresis and gel-permeation chromatography (GPC) (Jideani, Owusu, & Muller, 1994). The carbohydrates of acha have also been investigated (Jideani, Takeda, & Hizukuri, 1996).

The present study was undertaken to provide more understanding of the flavour of the cereal. Many similar flavour studies have been concentrated on major cereals such as rice (Buttery, Ling, Juliano, & Turnbaugh, 1983; Buttery, Turnbaugh, & Ling, 1988; Maga, 1984; Tava & Bocchi, 1999) and corn (Buttery, Ling, & Stern, 1997; Legendre, Dupuy, Ory & Mcllarth, 1978). Here we report on the identification of flavour compounds in cooked acha.

2. Materials and methods

Acha was obtained from a local market in Jos, Nigeria. Diethyl ether was freshly distilled through a 60-cm long

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Pyrex helice packed column, stored in the dark and protected by adding ca. 0.001% of Ethyl anti-oxidant 330.

2.1. Isolation of volatiles

D. exilis was cooked in the normal way (500 g of grain was added to 1 l of water and the mixture brought to the boil and held at 100 °C for 20 min). The freshly cooked acha (500 g) was immediately placed in a 2-l round bottom flask (containing an efficient magnetic stirrer) with 300 ml of odour-free water (20 °C). A quantity (10 ml) of a standard solution of 50 ppm 2-octanone (internal standard) in water was added. The volatiles were then isolated by a Tenax trap procedure similar to that described by Buttery et al. (1988). A Tenax trap (a Pyrex tube containing a 14×2.2 cm column of 60–80 mesh Tenax) and air inlet head were attached to the neck of the flask. The mixture was vigorously stirred, and purified air (3 l/min) was passed over the cooked acha slurry and led out of the flask through the Tenax trap. The isolation was carried out for 60 min; the trap was then removed and eluted with freshly distilled diethylether (50 ml). The ether extract was concentrated to approximately 10 μl with a warm water bath and Vigreux distillation column. This concentrate was used for the quantitative GC–MS analysis.

2.2. GC–MS analysis

Separation and identification of volatiles in the extract was carried out on a Shimadzu (Shimadzu, Kayato, Japan) QP-5000 system (GC–MS) equipped with a J & W Scientific DB-Wax column (30 m×0.25 mm i.d, 0.25 μm film thickness). A volume of 2 μl of extract was injected. Oven temperature was held at 35 °C for 5 min and then increased at a rate of 8 °C/min up to 280 °C, where it was held for between 25 and 35 min. The GC–MS system had a split ratio of 16:1 and a constant flow rate of 1.3 ml/min. Identification was carried out by probability based matching mass spectra in the G1033A NIST PBM Library (Hewlett-Packard, Palo Alto, CA). All extracts were injected in duplicate.

2.3. GC-sniffing

GC-sniffing was carried out using a Hewlett-Packard 5890 GC, equipped with an SGE olfactory detector outlet 0D0-1, using the same type of column and the same GC-settings, except that splitless injection was used. The normal FID-detector was detached and the total flow was led to the olfactory outlet. Extracts were sniffed by four judges. Each judge sniffed each extract once using the GC odour profiling technique (Tonder, Petersen, Poll, & Olsen, 1998). They were instructed to note the starting time of each odour, make a description of the odour quality (using descriptors of their own choice), and evaluate the intensity of the odour on a scale from 0–5. Each sniffing session continued for 40 min. To acquaint the judges with the sniffing technique they were trained once using a mixture of seven reference compounds (pentanal, hexanal, nonanal, ED-2-heptenal, benzaldehyde, 2, 4-nonadienal, 2-acetylpyrroline), which have all been found in most cereals.

Since the detector was detached from the sniffing-GC, the standard mixture used for training was also analysed by the GC–MS. Sniff-retention times were then corrected to match GC–MS retention times by linear interpolation.

3. Results and discussion

The results of GC–MS analyses of the volatiles obtained from cooked acha are shown in Fig. 1 and Table 1. Approximately 23 peaks were detected in the profile, and structures have been assigned to all these compounds on the basis of mass spectra data (Table 1). The compounds identified include three alcohols, five aldehydes, a ketone, six heterocyclic compounds, an ester, a terpene, two hydrocarbons, two benzene compounds and others.

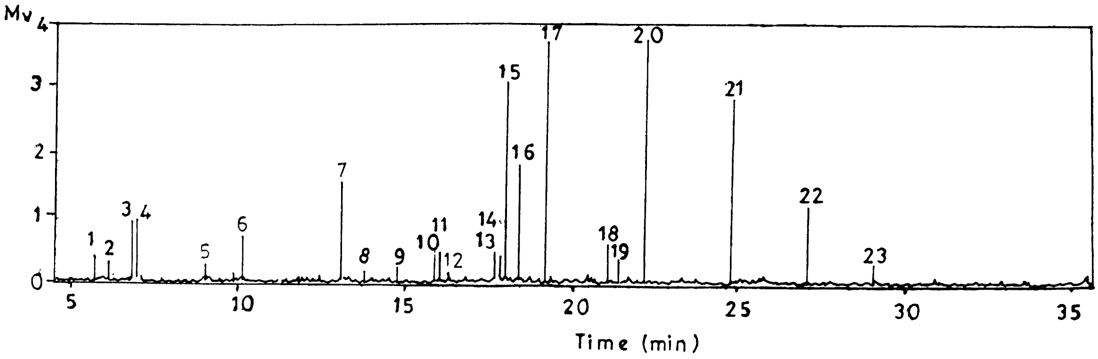

Fig. 1. Gas chromatogram of flavour volatiles identified in cooked acha. Peak numbers correspond to those of the compounds in Table 1.

The volatiles with the major peaks comprised ethylbenzoate, 2-pentylfuran, 2, 5-dimethylpyrazine, trisiloxane, 2, 6-dimethylpyrazine, and 1, 4-cyclohexadiene. Smaller peaks included 4-vinylguaiacol, 2-acetylpyrroline, 2-methylpyrazine, toluene, pentanal, nonanal, silicate anion tetramer and 3-cyclohexen-l-ol. Many of these volatile compounds have been shown to be products of lipid oxidation, Maillard reactions and other nonenzymic reactions (Maga, 1982). Heterocyclic compounds represented the most abundant class in cooked acha. For instance, the pyrazines have been recognized as important flavour constituents of a large number of cooked, roasted and toasted foods (Maga, 1982).

Many studies (Rizzi, 1972; Whitfield, 1992) have shown that a number of amino acids readily react with monosaccharides to form alkylpyrazines, and acha contains substantial amounts of these amino-acids and monosaccharide precursors. For instance, acha contains significant levels of glutamic acid and leucine (Hag & Ogbe, 1995). The role of glutamic acid and leucine in alkylpyrazine formation has been demonstrated by Wong and Bernhard (1988) and Arnoldi, Arnoldi, Baldi, and Griffini (1988). It is probable that these amino acids (glutamic acid and leucine), found in acha, could have contributed to the formation of some of the alkylpyrazines detected in the cooked acha. Qualitatively, the pyrazines detected in cooked acha were similar to those found in cooked rice (Buttery et al., 1988), but there were still some differences quantitatively.

Other browning volatiles detected, such as 2-acetyl-l-pyrroline, 2-pentylfuran, benzaldehyde, have been reported in cooked rice (Buttery et al., 1983), fresh and spray-dried 'masa' dough (Karahadian & Johnson, 1993) and 'kunun zaki' (Lasekan & Lasekan, 2000). 2-Acetyl-l-pyrroline was first reported as an important aroma component of aromatic rice (Buttery et al., 1988) and its occurrence in wheat bread crust (Schieberle, 1991), popcorn (Schieberle & Grosch, 1985) and rice cake (Buttery, Orts, Takeoka, & Nam, 1999) has also been reported. Proline, a precursor of 2-acetyl-l-pyrroline (Schieberle, 1989), is also abundant in acha (Haq & Ogbe, 1995) and its Strecker degradation product, l-pyrroline (Yoshikawa, Libbey, Cobb, & Day, 1965), has been shown to react readily with sugar degradation products to form 2-acetyl-l-pyrroline (Schieberle, 1989).

Important products produced by oxidative cleavage of lipids of the cereals include hexanal, decanal, nonanal and pentanal (Moio, Dekimpe, Etievant, & Addeo, 1993). 2-Pentylfuran is another volatile product of autoxidation of linoleic and linolenic acids (Sayaslan, Chung, Seib, & Seitz, 2000) and has been reported in extruded triticale (Pfannhauser, 1993) and cooked cereal and tuber starches (Sayaslan et al., 2000). Also, benzaldehyde a thermal reaction product of deca-2, 4-dienal and hexanal (Pfannhauser, 1993) has been reported in rye bread crusts (Schieberle & Grosch, 1985).

Two of the compounds reported in Table 1 are benzene compounds (dimethylbenzene and toluene). These

Table 1
Volatile compounds in cooked acha

Peak no.	Compunds	Odour description	Retention time	Peak area (%)[a]
1.	Toluene	Plastic, glue-like	5.71	1.7
2.	Pentanal	Green, almond	6.11	1.4
3.	Hexanal	Green grass	6.80	4.5
4.	Decanal	Burnt plastic	6.95	5.4
5.	Hexanol	Hot-paper, malodour	9.01	1.4
6.	l-Limonene	Turpentine-like	10.12	3.2
7.	1, 4-cyclohexadiene		13.07	6.4
8.	Nonanal	Slightly-rancid	13.76	0.8
9.	4-Vinylguaiacol		14.74	1.1
10.	Benzaldehyde	Almond-like	15.87	2.5
11.	Dimethylbenzene	Musty, astringent	15.99	2.9
12.	3, Cyclohexen-l-ol		16.30	0.9
13.	Benzylalcohol	Flower, fruity, citrus	17.66	2.2
14.	2-Methylpyrazine	Nutty, roasty	17.84	1.6
15.	2, 5-Dimethylpyrazine	Earthy raw, potato sweet	18.02	17.6
16.	2, 6-Dimethylpyrazine	Pleasant roasty	18.38	9.7
17.	Ethylbenzoate		19.22	38.3
18.	Hexan-2-one		21.07	3.1
19.	2-Acetylpyrroline	Cracker-like	21.36	1.7
20.	2-Pentylfuran	Caramel-like, sweet	22.19	38
21.	Trisiloxane		24.81	16.2
22.	Tetradecamethyl heptasiloxane		27.09	5.5
23.	Silicate anion tetramer		29.09	1.4

[a] Mean of two determinations.

Table 2
Results from GC-sniffing of cooked acha

Adjusted sniff-retention time (min)	Description of odour	No. of judges detecting odour	Average sniff intensity[a]	Identification GC–MS retention time (min)
5.70	Plastic, glue	1	0.5	
6.14	Green, almond, marzipan	2	1.6	Pentanal (6.14)
6.81	Green, grass	4	1.9	Hexanal (6.81)
7.12	Boiled potato	1	0.7	
9.03	Hot paper, foot malodour	2	1.7	
10.22	Turpentine	1	0.4	Hexanol (9.02)
13.31	Baked potato, chip	1	0.3	
13.74	Rancid, boiled potato	3	0.9	Nonanal(13.74)
14.81	Licorice	1	0.1	
15.89	Almond-like	4	3.1	Benzaldehyde (15.89)
16.01	Earthy, musty	2	1.4	
16.37	Fruity, sweet	3	1.0	
17.82	Nutty, roasty	2	2.9	2-Methylpyrazine (17.84)
18.01	Roasty, sweet	2	2.1	2,5-Dimethylpyrazine (18.02)
18.35	Pleasant roasty	3	1.3	2,6-Dimethylpyrazine (18.35)
19.42	Cheese	1	0.5	
21.11	Buttery, earthy	2	1.2	
21.37	Cracker-like, rice-like	3	2.4	2-Acetylpyrroline (21.36)
22.19	Caramel, burnt, sweet	2	1.9	2-Pentylfuran (22.19)
24.88	Rancid, musty	1	0.4	
27.12	Chocolate, burnt	1	0.9	
29.15	Astringent	2	1.3	

[a] Average sniff intensity.

compounds have been reported in cooked cereal starches (Sayaslan et al., 2000).

Other volatile compounds found, and not previously described in cereal products, include trisiloxane, tetradecamethyl-heptasiloxane and silicate anion tetramer. With the exception of silicate anion tetramer, the other compounds were probably impurities from the non-polar fibre used during extraction.

During GC-sniffing, 10 of the identified volatiles could be detected by two or more of the judges (Table 2). For an aroma signal to be assigned to a given GC-peak, the corrected sniff-retention time should correspond to a compound identified by GC–MS, and the description of the aroma quality should be compatible with that given in the Literature (Fenaroli, 1995). In the present study, recognizable aroma descriptions were obtained for each of the following at the appropriate retention times: pentanal, hexanal, hexanol, nonanal, benzaldehyde, 2-methylpyrazine, 2, 5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-acetylpyrroline and 2-pentylfuran.

4. Conclusion

Twenty-three volatile compounds were detected in cooked acha. The volatiles could conveniently be classified into three main groups: compounds that were formed by the degradation of starch, compounds formed by reaction between starch and protein and those resulting from lipid oxidation. In the present study, 10 compounds pentanal, hexanal, hexanol, nonanal, benzaldehyde, 2-methylpyrazine, 2, 5-dimethylpyrazine, 2, 6-dimethypyrazine, 2-acetylpyrroline and 2-pentylfuran) were identified as potential contributors to the flavour of cooked acha.

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