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The volatile components of wild ginger (Siphonochilus aethiopicus (Schweinf) B.I Burtt)

Ngozichukwuka P. Igoli^{1*} and Zak Obanu²

¹Department of Science, College of Advanced and Professional Studies, Makurdi, Benue State, Nigeria. ²Department of Food Science and Technology, University of Nigeria, Nsukka, Enugu State, Nigeria.

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Volatile components were isolated from the matrix of fresh and roasted samples of wild ginger (Siphonochilus aethiopicus (Schweinf) B.L Burtt) by solvent extraction and vacuum distilled. Quantitative determination of the volatiles in the distillate was done by GC-FID and organoleptic examination by GC-olfactometry. The sesquiterpenes were the major components of fresh wild ginger having a weight percent of 70 as against the monoterpene percentage of 3.5 and diterpene percentage of 25. The distillates obtained contained no ditepenes, while the monoterpene percentage increased to 72 in the fresh sample and 49 in the roasted sample. The sesquiterpene weight percent of the distillates decreased to 16 in the fresh sample and 27 in the roasted sample. Methyl-2-/-3-methyl butanoates, propyl-2-methylbutanoate, β-phellandrene, 2-isopropyl-3-methoxypyrazine, methoxypyrazine, methional, furanodiene and curzerenone were odorants important for the flavour of the fresh sample having the higher FD-factors. Curzerenone and furanodiene were characterised by NMR and GCMS after isolation from the crude solvent extract. 2-Acetylthiophene together with these eight odorants was strongly involved in the characteristic pleasant flavour of the roasted spice. The lowest odour threshold value of curzerenone detected was 0.8 to 1.69 µg/L_{air.}

Key words: Siphonochilus aethiopicus, flavour, terpenes, curzerenone.

INTRODUCTION

Wild ginger (*Siphonochilus aethiopicus* (Schweinf) B.L Burtt) is an herb of the Zingiberaceae family growing in the middle belt region of Nigeria. Its perennial tuberous roots give rise to annual leafy shoots which grow to about 35 cm high after flowering and are common throughout the West African region and elsewhere in tropical Africa (Burkill, 2000). It starts flowering from the onset of the rainy season in April and the flowers are purple with white corolla tubes. The South African varieties however flower between October to February giving faintly scented flowers that are white to bright pink (Kiew, 1980).

The rhizome is used as a spice by the Igede people of Benue State of Nigeria to eat yam which is a staple food crop and the flavour of the rhizome is enhanced by plant with a view to isolating the characteristic flavour components and identifying the potent odorants. The roasting (Igoli et al., 2005). This practice prompted our investigation of the fresh and roasted rhizomes of the South African variety of this spice wild ginger, (S. aethiopicus) has been reported as having a low content of monoterpenoids and containing two sesquiterpenoids: $4a\alpha H-3,5\alpha,8a\beta$ -trimethyl-4,4a,8a,9-tetrahydro-

naphtho[2,3b]- furan-8-one and 2-hydroxy-4a α H-3,5 α ,8a β -trimethyl-4,4a,8a,9-tetrahydro-naphtho [2,3b]-furan-8(5H)- one as the major constituents (Holzapfel et al., 2002).

The Nigerian variety which has not been studied organoleptically contains the sesquiterpenes epicurzerenone and furanodienone and the diterpenes 8(17), 12E-labdadiene-15, 16-dial, 15-hydroxy-8(17), 12E-labdadiene-16-al and 16-oxo-8(17), 12E-labdadiene-15-oic acid (Igoli et al., 2011). The aroma extracts dilution analysis (AEDA) employing the gas chromatography/olfactometry (GC/O) technique which has taken the place of gas chromatography-mass spectrometry (GC-MS) in organoleptic evaluation was used (Acree, 1997; Guth, 1996; Ullrich and Grosch, 1987). Aroma extracts are

^{*}Corresponding author. E-mail: ngozi_igoli@yahoo.com. Tel: +44(0) 141 5482360. Fax: +44(0) 141 552 2562.

diluted several times in succession, each time by a factor of 2, chromatographed and sniffed. The results are expressed as flavour dilution (FD) factors. An odorant with a high FD factor can be judged as an important contributor to the characteristic flavour of the food (Song et al., 2000; Grosch, 1993; Milo and Grosch, 1993). We hereby report on the potent odorants present in the spice and their quantitative determination. The sesquiterpene odorants: curzerenone and furanodiene were isolated from the plant for the first time. These were of the elemane and germacrane types, respectively and curzerenone has its odour quality/threshold value evaluated.

MATERIALS AND METHODS

Plant material collection/isolation of volatiles

Fresh rhizomes of wild ginger (*S. aethiopicus* (Schweinf) B.L Burtt) were harvested from the university farmlands of the University of Agriculture, Makurdi, Benue State of Nigeria in April 2001. The plant was authenticated by the Department of Forestry and Wildlife of the University where a voucher specimen n° 172 was deposited in the University of Agriculture Forest Herbarium. Some of the rhizomes were roasted in a Heraeus type T-5050 oven at 110°C for 24 h.

Three replicates of 5 g each of the fresh and roasted rhizomes were homogenised in 100 mL of 0.1 mol/dm³ CaCl₂.2H₂O solution and extracted with 100 mL of 1:1 pentane-Et₂O. The samples from the fresh extract were pooled together as were all those of the roasted. The pooled fresh and roasted samples were each distilled cryogenically under high vacuum (4 mPa) according to Guth and Grosch (1989) to isolate the volatiles from the non-volatile fraction, while the un-distilled fresh solvent extract served as a control. The distillates were concentrated on a Vigreux-column (50 × 1 cm) at $40\,^{\circ}\!\text{C}$ to $100\,\,\mu\text{L}$ expressed as a flavour dilution (FD)-factor = 1. Dilutions each by a factor of 2 to FD-factor 200 were made in pentane.

GC-FID analysis

For gas chromatographic separations, a Carlo Erba HRGC 5160 Mega series with an MFC 500 programming unit and EL Fisons electrometer (Carlo Erba, Hofheim, Germany) was used. Peak areas were integrated with a Merck Hitachi D-7500 integrator (Darmstadt, Germany). 1 µL portions were injected on column at 35 °C, the sniff port at 200 °C and the FID temperature set at 220 °C. Two columns: a non-polar DB-5 (30 m \times 0.25 mm; i.d., 0.25 μ m, J and W Scientific Inc., California, USA) and a polar DB-FFAP (30 m × 0.25 mm; i.d., 0.25 μm, J and W Scientific Inc., California, USA), each connected to a 2 m deactivated precolumn were used. The carrier gas was helium at a pressure of 80.00 KPa and flow rate of 2.0 mL/min. The temperature programme for DB-5 was that the oven at 35 °C was held isothermally for 1 min, raised at 40 °C/min to 60 °C, isothermal for 1 min then raised further at 8 °C/min to 290 °C and held isothermally for 15 min while that for DB-FFAP started at 35°C, isothermal for 1 min, raised at 40°C/min to 60°C then held isothermally for 1 min and raised further at 8°C/min to 240°C and isothermal for 15 min. Quantification of compounds from the concentrations of 0.050, 0.100, 0.200, 0.400, 0.800 mg/ml and the diterpene 8(17), 12E-labdadiene-15, 16-dial at 0.010, 0.020, 0.040, 0.080, 0.160 mg/mL were used as calibration factors for the undistilled fresh solvent extract. Three analyses were carried out on

each extract, the standard deviation determined and it was assumed that the response factor was equal to one for all the components. Retention indices of the components were determined by running each sample with a hydrocarbon mixture (Supelco, Pennsylvania, USA) from heptane to triacontane using the same parameters for the two column materials.

GC-O and AEDA

Sniffing test and AEDA were carried out on the distillates according to the method of Grosch (1993). The FD-factors of the flavour components were determined by AEDA. The odour active components in the different dilutions of the fresh and roasted samples of the spice were determined by sniffing, using DB-5 and DB-FFAP columns under the conditions described in the foregiong for the GC-FID. A panel of olfactorically trained chemists was used for the flavour description. The odour threshold value in air of one of the odorants and curzerenone was determined using pentadecane as an internal standard on a DB-5 column.

GC-MS analysis

The mass spectra was determined on a Hewlett Packard GC-HP 5890 series II chromatograph using a Hewlett Packard 5971 mass selective detector (Hewlett Packard, Palo Alto, CA, USA) and a DB-FFAP column using the conditions described in the foregoing. The electron impact voltage or ionisation voltage was 70eV. The volatile compounds were identified by both chromatographic and mass spectroscopic methods. Linear retention indices on both the polar and apolar columns were compared with published data and the 6th Wiley mass spectral data library was also used for automatic identification of GC-MS peaks.

Chromatographic isolation of constituents and NMR

Finely ground roasted samples (90 g) was extracted with a 1:1 pentane-diethyl ether mixture to yield 2.3 g of crude extract which was purified by column chromatography (silica gel 60; 0.063 to 0.2 mm; Merck) with 95:5 pentane-diethyl ether as eluting solvent in a water- cooled glass column (30 \times 1.5 cm) at a temperature of 10 $^{\circ}\mathrm{C}.$ Subsequent HPLC with a LiChrospher® Si 60 column (5 $\mu m;$ 250 \times 4.6 mm; Darmstadt, Germany) yielded curzerenone (20 mg). Lachrom Merck Hitachi L-7100 pumps A and B (Darmstadt, Germany) at a flow rate of 2 ml/min, a Lachrom Merck Hitachi L-7400 UV detector at 270 nm and a Merck Hitachi D-7500 integrator were used. Column chromatography of 10 g of crude hexane extract of the fresh sample using the conditions above isolated furanodiene (12 mg). The $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR (400 MHz) spectra were run in a JEOL (Tokyo, Japan) spectrometer using CDCl3 as solvent and TMS as internal standard.

RESULTS

The volatile oil obtained from solvent extraction was 1.17% of the fresh rhizome. The GC-profile of the undistilled fresh solvent extract is shown in Figure 1. It therefore contained 70% of sesquiterpenes, 25% of diterpenes and 3.5% of monoterpenes. The quantitative data is given in Tables 1 and 2 respectively report the relative GC-FID chromatographic peak areas of the volatile components of the distillates from the fresh and

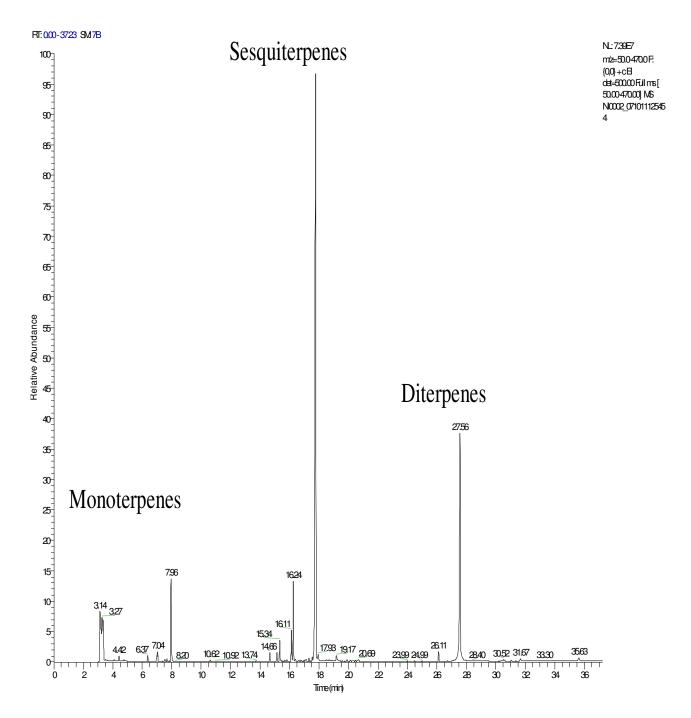


Figure 1. GC profile of the un-distilled fresh wild ginger extract.

roasted samples. It also shows the flavour profile got from the aroma extract dilution analysis. The higher volatilization of smaller molecules resulted in the distillate being enriched with monoterpenes and devoid of diterpenes after vacuum distillation. Thus in the distillate, the monoterpene percentage increased to 72 in the fresh sample and 49 in the roasted sample. The sesquiterpene weight percent consequently decreased to 16 in the fresh sample, 27 in the roasted sample. Figure 2 shows the

GC-profiles of the fresh and roasted samples distillates with numbered peaks of components for interpretation of identity. The fresh distillate showed 23 odorants as against 24 from the roasted. 2-Acetylthiophene, a pungent smelling principle, was present in the roasted distillate but absent in the fresh distillate. These aromas are classified as 1 aldehyde, 2 esters, 2 pyrazines, 18 terpenes and 1 thiophene.

AEDA showed that 8 odorants contributed more to the

Table 1. Volatile components of fresh wild ginger distillate.

Peaks	Component	Retention Index DB-5	Retention Index DB-FFAP	FD-factor	Odour quality	Peak area (%)
1	Methyl-2-/3-methylbutanoate	774	1021	180	Sweet/ fruity	Tr
2	Methional	905	1449	10	Potato-like/ roasty	Tr
3	α-Pinene	937	1034	1	Pine/woody	Tr
4	α-Fenchane	942	1032	1	Woody	3.64±0.14
5	Propyl-2-methylbutanoate	945	1043	90	Sweet/fruity	Tr
6	Camphene	957	1078	1	Fresh/clean	2.34±0.12
7	ß-Pinene	983	1137	1	Pine/woody	15.29±0.26
8	ß-Myrcene	987	1126	1	Citrus-like	5.24±0.09
9	α-Phellandrene	996	1169	1	Peppery/ citrus-like	4.15±0.15
10	δ-3-Carene	1013	1172	1	Citrus-like	2.78±0.08
11	p-Cymene	1020	1163	1	Citrus, Iemon-like	3.07±0.07
12	ß-Phellandrene	1045	1228	140	Minty/peppery/ citrus-like	35.03±0.03
13	2-Isopropyl-3-methoxy-pyrazine	1100	1423	30	Earthy/ roasty	Tr
14	2-Isobutyl-3-methoxy-pyrazine	1181	1517	30	Earthy/ roasty	Tr
*15						
16	α-Cubebene	1354	1556	1	Woody/ sweet	Tr
17	γ-Elemene	1409	1568	1	Woody	1.01±0.20
18	ß-Caryophyllene	1420		1	Woody	Tr
19	α-Humulene	1445	1568	1	Woody	5.98±0.23
20	Germacrene D	1484		1	Dry-woody/ spicy	Tr
21	ß-Bisabolene	1493		1	Dry-woody/ spicy	Tr
22	Germacrene B	1509		1	Woody	3.22±0.08
23	Furanodiene	1580	1876	10	Mushroom/ metallic	4.86±0.06
24	Curzerenone	1637	2300	10	Sweet/honey/ coconut-like	1.46±0.03
	Monoterpenes					72.02±0.05
	Sesquiterpenes					16.35±0.48

^{*15} odorant absent in the fresh spice. Tr- Trace or negligible. Peak area % mean ± std deviation.

flavour of the fresh spice and 9 odorants including 2-acetylthiophene were important for the flavour of the roasted spice. There were 9 monoterpenes and 9 sesquiterpenes out of which only one significant for the odour of the rhizome monoterpene and two sesquiterpenes were significant for the odour of the rhizome. The

monoterpene β -phellandrene and the sesquiterpenes curzerenone and furanodiene were important for the odour of the spice as they had high FD-factors. The sweet/fruity ester flavours, methyl-2-/-3-methyl butanoates were the most important odorants perceived at the highest dilution in the fresh sample distillate. These are

followed by β -phellandrene, which has a minty/peppery flavour. Another ester, propyl-2-methylbutanoate, a sweet/fruity apple flavour follows in prominence before the roasty/earthy smelling pyrazines. The sesquiterpenes curzerenone (sweet/coconut-like) and furanodiene (mushroom-like) were perceived at the next

Table 2. Volatile components of roasted wild ginger distillate

Peaks	Component	Retention index DB-5	Retention index DB-FFAP	FD-factor	Odour quality	Peak area (%)
1	Methyl-2-/3-methylbutanoate	774	1021	50	Sweet/ fruity	Tr
2	Methional	905	1458	10	Potato-like/ roasty	Tr
3	α-Pinene	936	1035	1	Pine/ woody	Tr
4	α-Fenchane	942	1032	1	Woody	2.79±0.17
5	Propyl-2-methylbutanoate	943	1056	30	Sweet/ fruity	Tr
6	Camphene	957	1078	1	Fresh/ clean	2.64±0.19
7	ß-Pinene	983	1137	1	Pine/woody	8.20±0.26
8	ß-Myrcene	987	1126	1	Citrus-like	5.18±0.17
9	α-Phellandrene	996	1170	1	Peppery/ citrus-like	3.52±0.02
10	δ-3-Carene	1013	1172	1	Citrus-like	1.82±0.01
11	p-Cymene	1020	1163	1	Citrus/ lemon-like	2.09±0.02
12	ß-Phellandrene	1041	1223	140	Minty/ peppery	23.13±0.01
13	2-Isopropyl-3-methoxy-pyrazine	1100	1400	60	Earthy/ roasty	Tr
14	2-Isobutyl-3-methoxy-pyrazine	1184	1518	60	Earthy/ roasty	tr
15	2-Acetylthiophene	1192	1752	30	Pungent/ peppery	Tr
16	α-Cubebene	1355	1559	1	Woody/ sweet	Tr
17	γ-Elemene	1396	1568	1	Woody	2.31±0.01
18	ß-Caryophyllene	1420		1	Woody	Tr
19	α-Humulene	1445	1571	1	Woody	6.29±0.10
20	Germacrene D	1484		1	Dry-woody/ spicy	Tr
21	ß-Bisabolene	1493		1	Dry-woody/ spicy	Tr
22	Germacrene B	1509		1	Woody	3.79±0.06
23	Furanodiene	1584	1878	10	Mushroom/ metallic	6.52±0.12
24	Curzerenone	1637	2300	10	Sweet/honey/ coconut-like	8.46±0.33
	Monoterpenes					48.98±0.58
	Sesquiterpenes					27.35±0.61

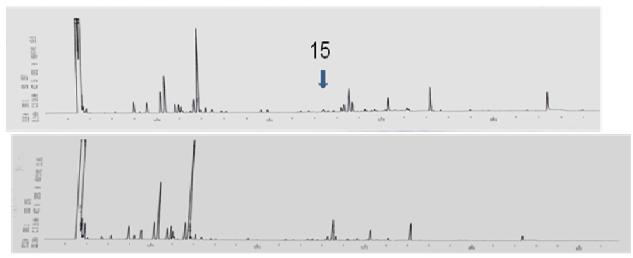
Tr-Trace or negligible. Peak area (%). Mean ± std deviation.

significant dilution together with the roasty/potato-like smelling methional.

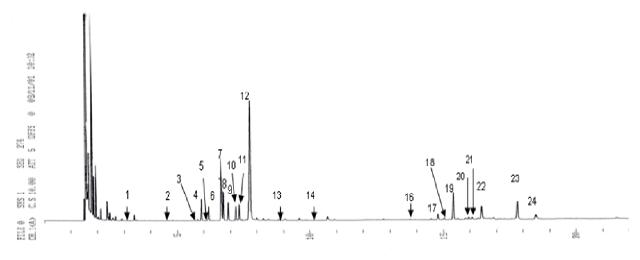
The most important odorant for the aroma of the roasted spice distillate was β -phellandrene, as the smaller-sized esters are extremely volatile and roasting would have reduced their concentration. The powerfully odorous pyrazines which were

more prominent in the roasted spice were next curzerenone, a significant odorant, had an odour threshold value of 0.8 to 1.69 $\mu g/L_{air.}$ The other 8 monoterpenes: α -pinene, α -fenchane, camphene, β -pinene, β -myrcene, α -phellandrene, δ -3-carene, p-cymene and 7 sesquiterpenes: α -cubebene, γ -elemene, β -caryophyllene, α -humulene,

germacrene-D, ß-before the sweet/fruity esters. Pungent smelling 2-acetylthiophene that was present only in the roasted spice was perceived at a higher dilution than the roasty/potato-like smelling methional and the sesquiterpenes, curzerenone and furano-diene. Sweet/coconutlike smelling Bisabolene and germacrene-D



DB-FFAP GC profiles: (Top) Roasted wild ginger distillate (Bottom) Fresh wild ginger distillate



GC profile of Fresh wild ginger distillate on DB-5.

Figure 2. Comparison of GC profiles of fresh and roasted wild ginger distillates on DB-5 and FFAP (Tables 1 and 2 for peak identity).

were only perceived without dilution. The ¹H and ¹³C NMR spectral data of curzereonone and furanodiene are shown in Table 3

while their structures 3a and 3b are shown in Figure 3

DISCUSSION

Terpenes were the major constituents of the volatiles of both the fresh and roasted rhizomes of wild ginger. The percentage of terpenes in the fresh un-distilled extract was 93.5% out of which sesquiterpenes were 70%, diterpenes 20% and monoterpenes 3.5%. Terpenes are also known to be the major constituents of the South

African variety of this spice wild ginger, which has a low content of monoterpenoids and high content of sesquiterpenoids (Holzapfel et al., 2002). The essential oils of other Zingiberaceous plants like the curcuma genus rhizomes, contain up to 87.1% terpenes as in *Curcuma sichuanensis* X. X. Chen out of which 1.5% were monoterpenes (Zhou et al., 2007). The essential oil of the Nigerian cardamom *Aframomum danielli* contains 96% monoterpenes and 1% sesquiterpenes (Adegoke et al., 1998). The essential oils of the leaves of other aframomum genus are dominated by monoterpenes while those from the rhizomes could either contain mostly monoterpenes or sesquiterpenes (Agnaniet et al., 2004; Baser et al., 2001). The results from wild ginger are

Table 3. 400 MHz 'H a	nd 13C NMR shifts of the	sesquiterpenes in CDCl ₃ .
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H-Position	Curzerenone	Furanodiene	C-Position	Curzerenone	Furanodiene
1-H	5.80 dd J=11,17.2 Hz	4.94 m	C-1	145.3 (CH)	134.9 (CH)
2-H	4.95d J=17.2 Hz	2.03 m	C-2	112. 1 (CH ₂)	30.0 (CH ₂)
2-H	4.95 d J=11.1 Hz	2.15 m	C-3	114.7 (CH ₂)	25.0 (CH ₂)
3-H	4.74 s	1.79 dt J=5.3 Hz	C-4	141.0 (C)	128.5 (C)
3-H	5.01 m	2.24 td J=3.5 Hz	C-5	63.7 (CH)	129.0 (CH)
5-H	3.01 s	4.7 dd J=7.9, 6.2 Hz	C-6	193.8 (C)	40.9 (CH ₂)
6-H		3.0 brd J=7.5 Hz	C-7	119.6 (C)	119.0 (C)
6-H		3.07 brd J=7.5 Hz	C-8	165.0 (C)	150.5 (C)
9-H	2.90 d J=17.6 Hz	3.43 d J=15.4 Hz	C-9	33.0 (CH ₂)	41.0 (CH ₂)
9-H	2.78 d J=17.6 Hz	3.53 d J=15.8 Hz	C-10	42.3 (C)	129.5 (C)
12-H	7.08 d J=1.32 H	7.07 d J=1.32 Hz	C-11	118.6 (C)	121.0 (C)
13- Me	2.18 d J=1.32 Hz	1.92 d J=1.32 Hz	C-12	139.1 (CH)	139.7 (CH)
14-Me	1.82 s	1.59 s	C-13	8.2 (CH3)	9.1 (CH ₃)
15-Me	1.18 s	1.27 s	C-14	24.2 (CH ₃)	16.8 (CH ₃)
			C-15	24.0 (CH ₃)	16.7 (CH ₃)

Comment [NK6]: All the proton positions are already identified.

therefore typical of the Zingiberaceae.

The contribution of a flavour compound to the aroma of a food is proportional to its FD-factor; the more potent the flavour, the higher its FD-factor (Ullrich and Grosch, 1987). The sweet/fruity ester flavours, methyl-2-/-3propyl-2-methylbutanoate, methyl butanoates and derivatives of the apple flavour (Bruice, 2007; Belitz and Grosch, 1999) were thus the most potent odorants. They contributed greatly to the characteristic pleasant aroma of the spice together with the sweet/honey/coconut-like The percentage sesquiterpene, curzerenone. curzerenone in the distillate increased from 1.47 in the fresh sample to 8.46 in the roasted sample. This could be due to the easy Cope rearrangement that germacrane sesquiterpenoids undergo to their elemane derivatives (Setzer, 2008; Colby et al., 1998). Thus, furanodienone, a constituent of the fresh crude extract of wild ginger together with epi-curzerenone (Igoli et al., 2011) could be rearranging to curzerenone under heat during roasting, thereby increasing its concentration.

The monoterpene, β-phellandrene, which has a minty/peppery/weak citrus-like odour, was very important for the aroma of wild ginger. It is also known to be important for the aroma of ginger and dill (Kirk, 1991). Methional had a roasty/potato-like smell while the pyrazines had roasty/earthy smells. These pyrazines are known to have a wide spectrum of aroma notes from paprika, chocolate, coffee, to potato smell and are present in paprika pepper and chillies (Belitz and Grosch, 1999; Kirk, 1991). These aromas, together with the pungent smelling 2-acetylthiophene present in the roasted spice make wild ginger milder than ginger (*Zingiber officinale* Roscoe) in the hot/pungent flavour. This is more so as there is a lack of gingerols, shogoals

and related compounds responsible for the high pungency of ginger (Connell, 1970). The flavour components were identified based on the Wiley mass spectral data and comparison of their retention indices with literature (Villanueva et al., 2009; Hanus et al., 2008; Zhou et al., 2007; Stoyanova et al., 2006; Alonzo et al., 2000; Khouri et al., 2000; Li and Jiang, 2004; Lis-Balchin and Roth, 2000; Mtiku et al., 2000; Pfeifhofer, 2000; Song et al., 2000).

The structures of curzerenone and furanodiene were confirmed by comparing the ¹H and ¹³C NMR spectral data and other NMR experiments like ¹H-¹H COSY, HMQC, HMBC, DEPT and NOESY with literature (Lorimer and Weavers, 1987; Brieskorn and Noble, 1982; Hikino et al., 1975; Rucker et al., 1971; Hikino et al., 1970). At least one of these sesquiterpenes has also been isolated from the rhizomes of *C. zedoaria* and *C. sichuanensis* X. X. Chen of the Zingiberaceae family, *Podocarpus spicatus* and the spice myrrh (Zhou et al., 2007; Lorimer and Weavers, 1987; Brieskorn and Noble, 1982; Hikino et al., 1975; Rucker et al., 1971; Hikino et al., 1970).

Twenty three odorants were identified in the fresh wild ginger (*S. aethiopicus* (Schweinf) B.L Burtt) while twenty four were identified in the roasted sample. These include the aldehyde methional, two esters, two pyrazines, eighteen terpenes and one thiophene. 2-Acetyl thiophene, a pungent smelling principle, which was present in the roasted spice but absent in the fresh spice makes the difference. The terpenes occur in such large amounts that in spite of relatively high odour thresholds, such as 0.8 to 1.69 µg/Lair for curzerenone, they are character impact compounds in wild ginger as in other spices like dill and ginger (Belitz and Grosch, 1999; Kirk,

1991).

The preference for the roasted spice over the fresh by the Igede people is because of its aroma. This is obviously due to the blend of the sweet smelling esters and terpenes, the roasty-smelling methional and pyrazines and the pungent smelling 2-acetylthiophene. It is therefore desirable that the extremely volatile components of both the fresh and roasted spice be studied further by static headspace analysis and olfactometry (SHA-O) to obtain a more comprehensive understanding of the odorants. This would be helpful if a simulation of the natural spice is considered using the major odorants. A further understanding of the thermal stabilities of the epimers of the character impact compound curzerenone could also be sought by molecular modeling.

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