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THE ESSENTIAL OIL OF GINGER FROM FIJI

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Key Word Index—*Zingiber officinale*; Zingiberaceae; ginger; essential oil; sesquiterpene hydrocarbons; citrals.

Abstract—The essential oil of ginger (*Zingiber officinale*) from Fiji was analysed by GC–MS and a number of sesquiterpenes not reported previously in ginger oil were identified including α-copaene, β-bourbonene, α-bergamotene, α-selinene, calamenene and cuparene. The composition of the oil was unusual in having a much higher neral and geranial content than oils reported from India, Australia, Japan and Africa.

INTRODUCTION

Ginger (*Zingiber officinale* Roscoe) is sold commercially as fresh rhizomes (green ginger), as preserved ginger, as a pungent extracted oleoresin, and as a steam-distilled essential oil. The composition of the essential oil components is an important factor in determining the quality of all four products [1]. Early workers identified zingiberene as the major constituent [2, 3]. Detailed studies have been conducted on the essential oils obtained from India [4] and from Australia [5–7] and a considerable differences in their compositions observed, particularly in the proportion of citrals.

Recent studies have examined the volatile constituents [8] and essential oil [9] from ginger in Japan and found a variation amongst samples of different ages and from different locations. Bednarczyk *et al.* [10–12] have identified the components characteristic of the flavours of ginger oil as α-terpineol, citral-a, citral-b, β-sesquiphellandrene, ar-curcumene, nerolidol and sesquiphellandrol.

We now report the identification of ginger oil constituents from Fiji and compare the composition with oils previously reported from other areas.

RESULTS AND DISCUSSION

Although Fiji only started exporting ginger on a large scale in 1963, primarily based on stock imported from India, China and Mauritius, Seeman reported seeing ginger in the Fiji Islands in 1981. Commercial ginger plants are not designated into cultivars and the rhizomes used in the present work were purchased at random from mature plants on sale locally.

The essential oil was prepared by maceration and steam distillation of the fresh green ginger and was formed in a relatively low yield (0.21–0.08 %) as a pale yellow mobile

Table 1. The composition of the major components in ginger oil from Fiji determined by GLC analysis

	Percentage of peak area					Reported percentage compositions of ginger oils from other areas			
			Fiji			Australia [7]	Others [7]†	India [4]	Japan [9]
Compound	A	B	C	D	E				
Cineole	10	9	6	8	6	—	—	1.3	4–11
Linalool	3	2	1	1	1	—	—	1.3	0.8–3
Unknown	3	2	1	1	1	—	—	—	—
Unknown	3	2	1	1	1	—	—	—	—
Neral	26	20	9	10	10	1–10	tr-1	0.8	8–27
Geranial	40	29	26	21	18	3–20	tr-3	1.4	12–36
Sesquiterpene hydrocarbons	13	36	30	50	57	34–62‡	48–85	66	12–23

* The samples Fiji A–E were fractionated on MS200/12500 columns operated at 120° for 10 min then 10°/min to 170°.
† Jamaica, Nigeria, Sierra Leone, China and Cochin.
‡ On storage up to 60 % of the volatile oil was ar-curcumene.

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oil with a strong sweet smell of citrals. Previous workers have reported yields of 2.2–0.5% based on dry weight or 0.5–0.1% based on wet weight [13].

The composition of the freshly prepared essential oil (Table 1) was different from that reported for oils from other areas. On the GLC column used for the initial analysis the hydrocarbons were not fully resolved and only tentative assignments could be made. On storage at 7° the pattern of the hydrocarbons changed, the peak assigned to ar-curcumene increased and the original major component was lost. A similar change was noted by Salzar [1] who suggested that ar-curcumene might be originally absent from ginger and be formed on storage by the decomposition of zingiberene and β-sesquiphellandrene which were almost completely lost after 1 month of exposure to air and light. A similar shift from zingiberene to ar-curcumene was also observed by Connell [7].

The values in the present work for the neral and geranial may include small (*ca* 10%) amounts of nerol and geraniol as these have almost identical retention times on the non-polar GLC column but were later resolved on a polar column.

The range of values reported in Table 1 cover different times of the year but all are based on mature rhizomes. The high (28–66%) proportion of neral and geranial is unusual and has not been consistently observed elsewhere. The studies by Connell [7] and Nigam [4] on oils from the traditional sources of India, China, Africa and Jamaica found a very low proportion (0–4%) of citrals, although this may in some cases be due to the method of preparation. Often scrapings, damaged rhizomes, or chipped and dried rhizomes are used and it has been found that drying before distillation reduces the lemon odour presumably because of loss of degradation of the citrals [13].

Samples from Australia characterized by a distinctive 'lemon', 'citrus-like' aroma, had a much higher (8–27%) proportion of citrals and contained a further unidentified oxygenated compound [7]. Comparison with the Japanese study [9] suggests that this component could be geranyl acetate, which was a major component in some oils. A similar peak was present in the Fiji oils but it could not be positively identified. The Japanese oils were very unusual as they covered a wide range of compositions depending on the location and time of harvest, but only a small number of samples were taken. As well as examples containing high proportions of neral and geranial (24–26%), some fresh rhizome (Shinshoga) samples contained high proportions of geraniol and geranyl acetate (over 40%). The proportion of zingiberene was also very limited (1–14%) in contrast to earlier reports of oil from India, which contained over 70% zingiberene [2, 3].

The oil from Fiji was most similar to the Japanese samples, Taneshoga and Oyashoga, which had a low geraniol–geranyl acetate content and 17–20% neral and 23–35% geranial. The Japanese and Fijian oils also contained a high proportion (4–11%) of 1,8-cineole which

Table 2. GC–MS analysis of the essential oil of ginger from Fiji

R_t	Peak height*	Compound	M^+ (*m/e*)	Reference to previous isolation from ginger
5.0	trace	α-pinene	136	[4, 8, 9, 15]
5.5	55	camphene	136	[2–4, 8, 9, 15]
6.5	4	β-pinene	136	[4, 8, 9, 15]
7.9	30	myrcene	136	[4, 8, 9]
9.2	20	limonene	136	[4, 8, 15]
9.4	230	1,8-cineole	154	[2–4, 8, 9, 15]
		β-phellandrene (minor)	136	[2–4, 8, 9, 15]
12.2	15	mixture		
12.7	67	methylheptenone	126	[2–4]
14.0	6	nonanone	142	
16.0	16	citronellal	154	
16.5	15	α-copaene	204	
16.8	120	linalool	120	[2–4, 9, 15]
17.8	5	mixture	152	
18.2	65	bornyl acetate	196	[4]
		undecanone	170	
19.5	>250	neral	152	[2–4, 7, 9–11, 15]
		α-terpineol (minor)	154	[9–11]
		borneol (minor)	154	[2–4, 9, 15]
20.5	145	geranial	152	[2–4, 7, 9, 11]
21.0	100	mixture (β-bisabolene and geranyl acetate)	156/204	
21.5	72	ar-curcumene	202	[2–4, 7, 9–11]
22.4	110	geraniol	154	[2–4, 9, 15]
25.4	25	nerolidol	222	[11]
26.0	6	elemol	222	
29.0	6	β-eudesmol	222	[1]

*Total ion monitor.

has not previously been considered to be a major constituent as less than 3% was found in Indian oils [4].

The peak assignments in the chromatograms of the oil from Fiji were carried out by fractionation of the oil by column chromatography to give three fractions: hydrocarbons, 1,8-cineole, which was identified by spectroscopic and chromatographic comparison with an authentic sample, and oxygenated compounds.

The hydrocarbons were separated by TLC to give ar-curcumene, sesquiphellandrene and β-bisabolene but no zingiberene could be isolated. A hydrocarbon, with a strong IR band at 890 cm^{-1}, was also isolated but it could not be identified from published sesquiterpene spectra [14] or by mass spectroscopy. The oxygenated fraction appeared to have undergone some decomposition on the column and was not studied further.

Direct preparative GLC of the total oil yielded neral, geranial and linalool, which were identified spectroscopically and by direct comparison on GLC, but again the sesquiterpenes were incompletely resolved and to a large extent suffered rearrangement to give ar-curcumene. Comparison of the GLC separations with those of Connell [6, 7] suggested that the initial major compound, which was lost on storage, was probably sesquiphellandrene rather than zingiberene. Although Masada [15] examined ginger oil from Japan by GC–MS, he only identified 16 of the 115 observed components and surprisingly he found only a very small peak for citral-a(neral) and did not assign a peak to citral-b(geranial).

Analysis by GC–MS on a Carbowax 20 M column of a sample of oil, which had been stored for 1 year at 7°, enabled most of the major components to be identified by their mass spectra [15–17]. Almost all have been reported previously in ginger oil (Table 2), although not always in the same sample, and often earlier identifications have not been fully described. As in the analyses on a non-polar column, the neral and geranial components dominated the chromatogram but in this system they unfortunately overlapped and obscured the peaks for the sesquiterpene hydrocarbons. The new compounds identified included nonanone, undecanone, citronellal, α-copaene and elemol. Octanal, nonanal and decanal although previously reported [15] were not observed. A number of previously reported compounds were not identified, including sabinene, Δ^3-carene [8], nerol [9], geranyl acetate [9] and linalyl acetate [15].

A separate examination of the hydrocarbon fraction from the stored sample by GC–MS permitted many of the sesquiterpenes to be identified (Table 3). Only a few of these compounds have been identified previously in ginger oils. Some of the identifications are tentative because of a lack of authentic mass spectra and are based on an agreement of the relative retention times with other studies (i.e. [18]) and the expected mass spectra. Surprisingly none of the peaks corresponded to zingiberene or sesquiphellandrene, either in retention times or mass spectra, suggesting that either these compounds had completely rearranged to ar-

Table 3. GC–MS of hydrocarbon fraction from ginger essential oil

R_t	Peak height*	Compound	M^+ (*m/e*)	Reference to previous isolation from ginger
3.0	5	$C_{11}H_{24}$	156	
3.6	10	β-pinene	136	[4, 8, 9, 15]
5.2	130	myrcene	136	[4, 8, 9]
6.4	>250	limonene	136	[4, 8, 15]
6.8	>250	1,8-cineole	154	[2–4, 8, 9, 15]
8.4	25	*p*-cymene	134	[4]
9.4	10	unknown		
11.4	10	$C_{14}H_{30}$	198	
12.0	15	unknown		
12.5	5	unknown		
13.5	10	δ-elemene	204	[4]
14.0	110	α-copaene	204	
14.8	10	β-bourbonene	204	
15.4	75	α-bergamotene	204	
16.4	180	β-elememe	204	[4]
16.8	40	caryophyllene	204	[15]
17.4	10	unknown		
18.0	180	*trans*-β-farnesene	204	[2, 4]
18.4	65	α-selinene	204	
18.8	65	(γ-amorphene)	204	
19.5	150 × 5	β-bisabolene	204	[2, 4, 7, 9]
20.8	70 × 5	ar-curcumene	202	[2–4, 7, 9–11]
22.5	30	calamenene	202	
25.6	30	caryophyllene oxide	220	
27.0	25	cuparene	202	

* Total ion monitor.

curcumene in storage or that only minor amounts had been present. The only other hydrocarbons which have been reported in ginger are sesquithujene, epizonane and zonane, found in an oil from India [19, 20], and γ-selinene [4]. There is also a report of β-zingiberene [4] but this is ill-defined and it may largely be a mixture of sesquiphellandrene and zingiberene [5]. The large number of sesquiterpene compounds found in the present work suggests that some of the compounds identified earlier by distillation and identified by degradation products may well have been mixtures.

The composition of the oil from Fiji is thus primarily unusual in containing a higher proportion of citrals than other ginger oils. One oil from Japan was found to have a similar composition but other Japanese oils showed a wide range from different locations. Together these results suggest that the composition of ginger oils may be dependent on a chemotaxonomic difference between strains or on climate and growing conditions, with a low citral content being found in India and Africa but higher in Australia and Japan, and highest in Fiji. However, some of the differences may be due to the handling of rhizomes before extraction and the storage of the sample.

EXPERIMENTAL

Essential oil. Fresh ginger roots from Suva Market, Fiji were shredded in a Waring blender and the slurry was steam-distilled to give after extraction of the distillate with EtOAc and evapn of the solvent the essential oil (0.08–0.21% based on wet weight). The oil (510 mg) was fractionated by dissolving in petrol (40–60) and running onto a short column of neutral Al_2O_3. Elution with petrol gave a hydrocarbon fraction (140 mg) and then with petrol–$CHCl_3$ gave cineole (12 mg). Further elution with $CHCl_3$ yielded an oxygenated fraction (113 mg).

Gas chromatography. Quantitative analyses were carried out using a dual-packed glass column chromatograph, fitted with FID detectors. The carrier gas was N_2 at 40 ml/min and columns (1.5 m × 3 mm) were packed with 3% OV101, 8% silicone fluid MS 200/12500, or 10% Carbowax 20M.

Gas chromatography–mass spectrometry. The carrier gas was He at 45 ml/min and the glass column (1.5 m × 3 mm) was packed with 10% Carbowax 20M on Universal B. The oven was programmed from 70 to 220 at 4/min.

Identification of components. The components of the oil were identified by GC–MS. The identities of the major components were confirmed by fractionation of the oil by repeated TLC on Si gel or by prep. GLC to give the individual compounds, which were examined by IR and ^1H NMR spectroscopy and comparison with authentic samples on GLC.

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REFERENCES

1. Salzar, U.-J. (1975) *Int. Flavours Food Addit.* **6**, 206.
2. Gildemeister, E. and Fr. Hoffman (1956) *Die Aetherischen Oele*, 4th edn, Vol. IV, p. 489. Academie, Berlin.
3. Guenther, E. (1952) *The Essential Oils*, 2nd edn, Vol. V, p. 106. Van Nostrand, New York.
4. Nigam, M. C., Nigam, I. C., Levi, L. and Handa, K. L. (1964) *Can. J. Chem.* **42**, 2610.
5. Connell, D. W. and Sutherland, M. D. (1966) *Aust. J. Chem.* **19**, 283.
6. Connell, D. W. (1970) *Flavour Ind.* **1**, 677.
7. Connell, D. W. and Jordan, R. A. (1971) *J. Sci. Food Agric.* **22**, 93.
8. Kami, T., Nakayama, M. and Hayashi, S. (1972) *Phytochemistry* **11**, 3377.
9. Sakamura, F. and Hayashi, S. (1978) *Nippon Nogei Kagaku Kaishi* **52**, 207.
10. Bednarczyk, A. A. and Kramer, A. (1971) *Food Technol. (Chicago)* **25**, 24.
11. Bednarczyk, A. A. and Kramer, A. (1975) *Chem. Senses Flavor* **1**, 377.
12. Bednarczyk, A. A., Galetto, W. G. and Kramer, A. (1975) *J. Agric. Food Chem.* **23**, 499.
13. Mathew, A. G., Krishnamurthy, N., Nambudiri, E. S. and Lewis, Y. S. (1973) *Flavour Ind.* **4**, 226.
14. Moshonas, M. G. and Lund, E. D. (1970) *Flavour Ind.* **1**, 375.
15. Masada, Y. (1976) *Analysis of Essential Oils by Gas Chromatography and Mass Spectrometry*, p. 251. John Wiley, New York.
16. Cornu, A. and Massot, R. (1971) *Compilation of Mass Spectral Data.* Heyden, London.
17. Stenhagen, E., Abrahamsson, S. and McLafferty, F. W. (1969) *Atlas of Mass Spectra.* John Wiley, New York.
18. Wenninger, J. A., Yates, R. L. and Dolinsky, M. (1967) *J. Assoc. Off. Analyt. Chem.* **50**, 1313.
19. T. Terhune, S. J., Hogg, J. W., Bromstein, A. C. and Lawrence, B. M. (1975) *Can. J. Chem.* **53**, 3285.
20. Anderson, N. H., Syrdal, D. D., Lawrence, B. M., Terhune, S. J. and Hogg, J. W. (1973) *Phytochemistry* **12**, 287.