Phytochemistry, Vol. 26, No. 8, pp. 2207–2212, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00

CHANGES IN VOLATILE CONSTITUENTS OF *ZINGIBER OFFICINALE* RHIZOMES DURING STORAGE AND CULTIVATION

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(*Revised received* 1 *February* 1987)

Key Word Index—*Zingiber officinale*; Zingiberaceae; ginger; rhizomes; volatile constituents; acyclic oxygenated monoterpenes; geranyl acetate; geraniol; geranial; neral; storage.

Abstract—The essential oil from the fresh rhizome of *Zingiber officinale* was characterized by the presence of acyclic oxygenated monoterpenes mainly composed of neral, geraniol, geranial and geranyl acetate. During storage the content of neral and geranial in the rhizome increased to *ca* 60% of the essential oil, while the content of geraniol and geranyl acetate decreased to an undetectable amount. The change resulted from the conversion of geranyl acetate into geraniol, geranial and neral, successively. The content of geranial and neral decreased to a small extent through cultivation of the stored rhizome, whereas a large quantity of geraniol and geranyl acetate occurred in the newly propagated fresh rhizome.

INTRODUCTION

Zingiber officinale is a perennial plant with tuberous rhizomes. The dried rhizomes are one of the most important spices. In addition, the essential oil and oleoresin from the rhizomes are utilized as flavour additives. Therefore, this plant is widely cultivated in tropical, subtropical and temperate regions.

Ginger rhizomes are roughly classified into three categories, such as the fresh rhizome (Shinshoga in Japanese), the propagation rhizome (Taneshoga) and the one-year-old rhizome (Oyashoga). The fresh rhizome is relished as garnishings because of the pleasant aroma. However, earlier investigations on the volatile constituents of ginger rhizomes were carried out on the essential oil from a commercial source of the dried rhizomes [1–7]. According to these reports, major constituents in the essential oil of the ginger rhizomes from other countries are sesquiterpenes. In contrast with these ginger rhizomes, the main constituents in the essential oil of the Japanese fresh rhizome were monoterpenes, which were predominantly composed of such oxygenated compounds as neral, geraniol, geranial and geranyl acetate [8]. Geranyl acetate has never previously been found in the ginger rhizomes, and the presence of such a high content of geraniol is the first case for ginger rhizomes though a trace amount of geraniol is found in the ginger oils from India [3] and from Sri Lanka [9]. Recent studies indicated that the essential oil of the fresh green ginger from Fiji had a high content of neral and geranial [10] and that the monoterpene content decreased with an increase in the sesquiterpene content on drying of the rhizomes [9]. The present work describes an investigation of the changes in volatile constituents of the fresh rhizome through storage and cultivation.

RESULT AND DISCUSSION

Volatile constituents of fresh rhizome

Compositions of the essential oils from the immature and mature fresh rhizomes of *Z. officinale* 'Oshoga' are shown in Table 1, indicating that both essential oils are mainly composed of acyclic oxygenated monoterpenes, such as neral, geraniol, geranial and geranyl acetate (60–70%) similar to those of other fresh rhizomes of the cultivar 'Oshoga' grown in Japan [8], and that the oil compositions of these immature and mature fresh rhizomes are similar to each other. However, a remarkable difference in the content of geranyl acetate is seen between both the rhizome oils. The rhizome from Japan is, in addition, characterized by the presence of car-3-ene, isoborneol, citronellol, nerol, aromadendrene and calarene.

Changes in volatile constituents of the fresh rhizome during storage

After harvest, mature fresh rhizomes are stored for several months under controlled conditions and then used not only as propagation rhizomes, but also as foods. To elucidate variations in volatile constituents during storage, the analysis of the constituents was carried out on the mature fresh rhizomes stored at 15° for one–five months and then at 23° for three months under high humidity in the dark. The volatile oil of these rhizomes stored for various periods was similar to the fresh rhizome oil in respects of not only the constituents but also the high content of the acyclic oxygenated compounds (95%) in monoterpenes. The total content of monoterpenes (77%) in the oil remained constant with a fluctuation within 5% of the mean (Fig. 1), but contents of the monoterpene aldehydes increased with a concomitant lowering in the amounts of monoterpene alcohols and esters during storage although contents of the other oxygenated monoterpenes, monoterpene hydrocarbons and sesquiterpenes changed little or slightly during the storage. The total content of neral and geranial increased to *ca* 60% of the oil in three months after storage, whereas the content of geraniol and geranyl acetate decreased to an undetectable amount after eight months storage. In addition, the ratios of neral and geranial and geraniol and geranyl acetate to the total monoterpenes gave a good hyperbolic relation to each other when plotted against the storage period

Table 1. Composition (%) of the essential oil from fresh rhizomes of *Z. officinale*

Constituent	Immature*	Mature*
Monoterpenes†‡	77.8	74.8
Hydrocarbons	2.5	3.6
Tricyclene	tr	0.1
α-Pinene	0.3	0.5
Camphene	2.1	1.7
β-Pinene	tr	0.8
Myrcene } Limonene }	tr	tr
Car-3-ene	0.1	0.5
β-Phellandrene	tr	tr
α-Terpinene	tr	tr
Oxygenated compounds	75.2	70.9
1,8-Cineole	7.3	9.2
Linalool	1.2	1.2
Isoborneol	0.8	1.2
α-Terpineol	0.5	1.3
Citronellol	tr	0.5
Nerol	0.1	2.0
Neral	8.1	9.7
Geraniol	13.0	16.1
Geranial	21.8	20.0
Geranyl acetate	22.4	9.7
Sesquiterpenes†‡	22.4	25.4
Hydrocarbons	20.0	20.1
α-Copaene	0.1	1.6
Aromadendrene	2.6	0.5
Guaiene	tr	0.1
Calarene	tr	0.1
β-Bisabolene	0.9	1.3
Zingiberene	8.9	11.1
α-Curcumene	5.1	1.9
β-Sesquiphellandrene	2.4	3.5
Oxygenated compounds	tr	1.2
Nerolidol	tr	0.3
β-Sesquiphellandrol	tr	0.9

*Immature: three-month-old plant rhizome; Mature: seven-month-old plant rhizome.

†Order of elution from an OV-17 GC column.

‡The figures include percentages of other unidentified compounds.

tr: trace (< 0.1 %).

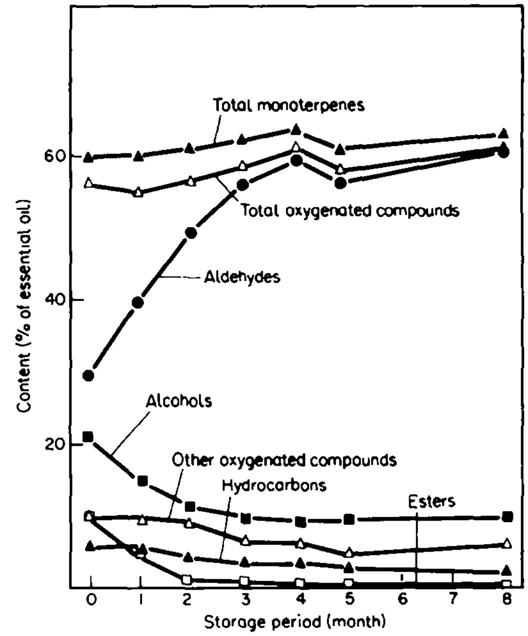

Fig. 1. Changes in monoterpene constituents of the fresh rhizome of *Z. officinale* during storage.

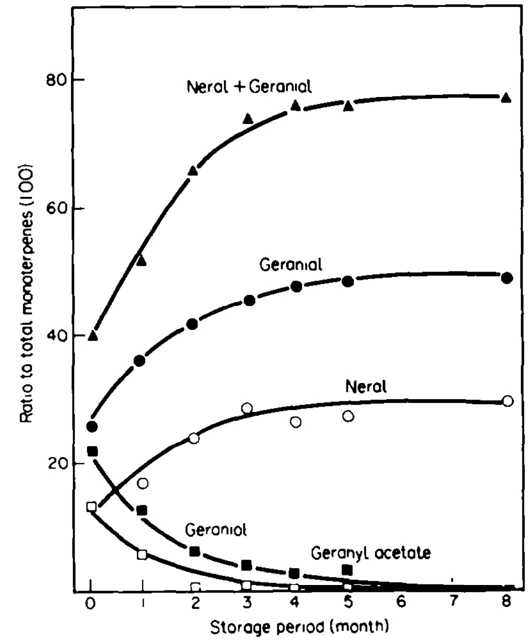

Fig. 2. Changes in the ratio of acyclic oxygenated monoterpenes to total monoterpenes in the fresh rhizome of *Z. officinale* during storage.

(Fig. 2). Thus, an increase in the content of neral and geranial was found to occur with a decrease in the content of geraniol and geranyl acetate during storage of the rhizome.

Although the moisture content in the fresh rhizome was kept constant during storage of the fresh rhizome, the weight of the rhizome and the essential oil yield lowered with lengthening of the storage period (Fig. 3). A change in the absolute amount of the volatile constituents (mg/100 g of fresh rhizome) was then followed by relating the change with the weight and the oil yield in the rhizome stored for each period. The absolute amount of the most volatile constituents decreased during storage. This decrease was attributed to the loss due to evaporation of the constituents. When the rate constants of evaporation are plotted against Kováts constant [11], a curve was obtained (Fig. 4). However, the rate constants of evaporation of geraniol and geranyl acetate greatly deviated from this curve. This deviation shows a decrease in the absolute amounts of geraniol and geranyl acetate. On the other

Table 2. Monoterpene constituents of shoots and their mother rhizome of *Z. officinale*

Constituent	Shoot % of oil	Shoot mg†	Mother rhizome* % of oil	Mother rhizome* mg†
Acyclic	81.7	1236	66.7	217
Myrcene‡	0.2	3	0.1	2
Linalool	1.3	20	1.2	4
Citronellol	0.8	12	1.2	4
Nerol	3.6	54	3.8	12
Neral	17.3	262	22.9	74
Geraniol	22.8	345		
Geranial	35.3	534	37.5	121
Geranyl acetate	0.4	6		
Monocyclic	6.6	101	8.1	27
Limonene	tr	tr		
β-Phellandrene	tr	tr		
α-Terpinene	0.1	2	0.1	2
1,8-Cineole	4.8	73	5.7	18
α-Terpineol	1.7	26	2.3	7
Bicyclic	1.6	25	3.5	24
Tricyclene	0.6	9	0.2	3
α-Pinene	0.1	2		
Camphene	0.1	2	0.5	8
β-Pinene§	0.2	3	0.1	2
Car-3-ene	tr	tr	0.2	3
Isoborneol	0.6	9	2.5	8
Total	90.4	1367	78.2	256

*Stored for eight months in the dark.
†mg/100 g dry wt.
‡Figures include percentages of β-pinene.
§Figures include percentages of myrcene.
tr: trace (< 0.1 % or 1 mg).

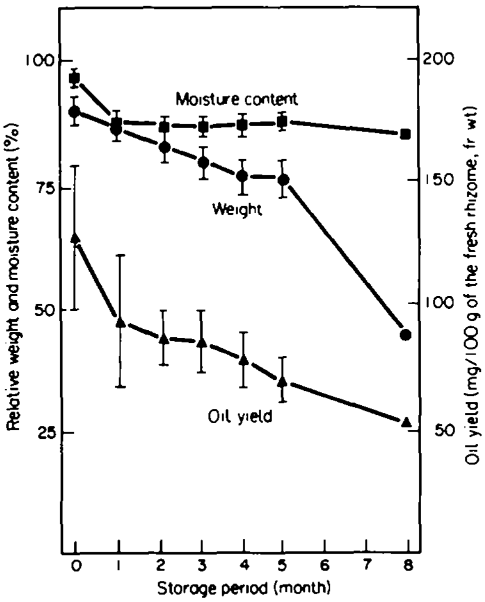

Fig. 3. Changes in the weight and moisture content of the fresh rhizome of *Z. officinale* and yield of the essential oil from the rhizome during storage.

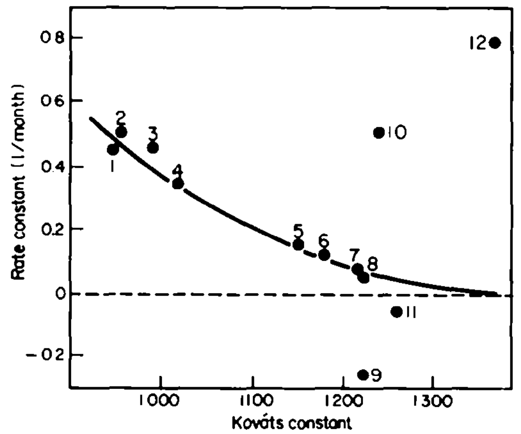

Fig. 4. Relationship between the rate constant of evaporation and Kováts constant in monoterpene constituents of the stored rhizome of *Z. officinale*. 1. α-Pinene 2. Camphene 3. β-Pinene 4. 1,8-Cineole 5. Isoborneol 6. α-Terpineol 7. Citronellol 8. Nerol 9. Neral 10. Geraniol 11. Geranial 12. Geranyl acetate.

hand, the deviation from the curve to the negative direction was recognized for the rate constants of evaporation of geranial and neral, indicating obviously an accumulation of both these terpene aldehydes. Thus, it is considered that geranyl acetate is hydrolysed into geraniol and the geraniol is oxidized to geranial and neral during storage of the rhizome.

Volatile constituents of the shoot

Etiolated shoots were formed on the rhizome during the eight months storage in the dark under the same conditions as described above. The shoots composed primarily of rhizomes accumulated *ca* four times as much essential oil as their mother rhizome. Constituents of the essential oil were analysed to compare the composition with those of the essential oils of the mother and fresh rhizomes. The essential oil of the shoots characteristically contained a high level of monoterpenes (90 %) composed mainly of the acyclic oxygenated compounds, neral, geraniol and geranial, but only a small amount of geranyl acetate (Table 2). The significant difference in the composition between the shoot oil and the mother rhizome oil is in the high content of geraniol (23 %) in the former, but the similarity in the composition between both the oils was in the high contents of neral and geranial and in the extremely low content of geranyl acetate. These results indicate that the young shoots produce little geranyl acetate, although the shoots produce not only geraniol but also neral and geranial.

Changes in volatile constituents of the stored rhizome during cultivation

To investigate changes in volatile constituents of ginger rhizomes with ageing, the rhizome, after storage for five months, was transferred to soil as the propagation rhizome and cultivated under natural light. After cultivation for seven months, newly propagated mature fresh rhizomes and their mother rhizomes were collected to analyse volatile constituents of these rhizomes. The essential oil of the propagation rhizome consisted of the same volatile constituents as those of the essential oil of the mother rhizome, but the composition of the propagation rhizome oil differed not only from that of the mother rhizome oil in having a higher content of geranial and neral, but also from that of the newly propagated fresh rhizome oil in having a higher content of neral and geranial and a lower one of geraniol and geranyl acetate (Table 3).

The distribution of neral, geraniol, geranial and geranyl acetate in blades and greenish upper and lower parts and

Table 3. Monoterpene constituents of cultivated rhizomes of *Z. officinale*

	Propagation rhizome*		Mother rhizome		Fresh rhizome	
Constituent	% of oil	mg†	% of oil	mg†	% of oil	mg†
Acyclic	64.6	452	53.6	359	60	438
Myrcene‡	0.2	1	1.8	12	2.0	15
Linalool	1.4	10	2.4	16	2.7	20
Citronellol	0.7	5	0.9	6	1.0	7
Nerol	2.8	20	1.9	13	2.3	17
Neral	20.2	141	17.4	117	13.3	97
Geraniol	3.1	22	5.1	34	12.1	88
Geranial	35.8	250	23.8	159	20.7	151
Geranyl acetate	0.4	3	0.3	2	5.9	43
Monocyclic	6.8	48	13.6	91	12.3	90
Limonene			tr	tr	tr	tr
β-Phellandrene			tr	tr	tr	tr
α-Terpinene	0.1	1	0.4	3	0.3	2
1,8-Cineole	4.3	30	11.2	75	10.1	74
α-Terpineole	2.4	17	2.0	13	1.9	14
Bicyclic	2.8	19	6.8	47	5.6	50
Tricyclene	0.1	1	0.7	5	0.5	4
α-Pinene	0.1	1	0.4	3	0.5	4
Camphene	0.4	3	1.3	9	1.6	12
β-Pinene§	0.2	1	1.8	12	2.0	15
Car-3-ene	0.2	1	0.4	3	0.4	3
Isoborneol	1.8	12	2.2	15	1.6	12
Total	75.5	528	75.3	506	79.6	590

*Stored for five months in the dark, planted and cultivated for seven months under natural light.

†mg/100 g dry wt.

‡Figures include percentages of β-pinene.

§Figures include percentages of myrcene.

tr: trace (< 0.1 % or 1 mg).

Table 4. Distribution of acyclic oxygenated monoterpenes in blades and sheaths of *Z. officinale*

			Sheath					
			Greenish					
	Blade		Upper		Lower		Reddish	
Compound	%*	mg†	%*	mg†	%*	mg†	%*	mg†
Neral	12.3	18	13.3	50	8.9	12	5.5	51
Geraniol	19.9	30	15.2	58	5.2	7	1.0	9
Geranial	18.3	28	20.8	79	13.2	17	8.4	78
Geranyl acetate	0.7	1	1.2	5	0.5	1	0.3	3

* % of the essential oil.
†mg/100 g dry wt.

reddish part of sheaths of the cultivated ginger plant was next studied. Neral, geraniol and geranial predominated in the essential oils of the blades and the greenish upper part of the sheaths, similar to the oil of the newly propagated fresh rhizome (Table 4). Relatively low levels of the three compounds were observed in the oils of the other greenish lower and reddish parts of the sheaths. The content of geranyl acetate, however, was low in the oils from all parts of the blades and the sheaths. The reddish sheath oil was characterized by large amounts of other higher boiling compounds (72%) composed of sesquiterpenes.

In conclusion, the essential oil from the fresh rhizome was characterized by a high content of the four acyclic oxygenated monoterpenes, geraniol, geranyl acetate, neral and geranial. The content of neral and gernial increased to *ca* 60% of the essential oil during storage of the rhizome, while the content of geraniol and geranyl acetate decreased to an undetectable amount. Such changes resulted from the conversion of geranyl acetate into geraniol, geranial and neral, successively. During cultivation of the stored rhizome, however, the content of geranial and neral decreased to a small extent, whereas a large amount of geraniol and geranyl acetate occurred in the newly propagated fresh rhizome in this order. Geranyl acetate seems to be a characteristic compound of the fresh rhizome.

EXPERIMENTAL

Methods of storage and cultivation of ginger. Immature and mature rhizomes of *Z. officinale* Rosc. 'Oshoga' were harvested in July and November, respectively. Storage experiments were carried out as follows. Mature fresh rhizomes (*ca* 60 kg) were air-dried for 2 days at room temp., carefully brushed to remove soil and divided into groups weighing *ca* 500 g each. Each group was put in a net sack. The material was kept in a storage chamber at 15° under high humidity (over 95%) until April. Several groups were taken out of the chamber at 30 day-intervals and separately subjected to analysis as described below. Part of the groups, after storage for five months under the conditions mentioned above, was kept at *ca* 23° under high humidity for three months. Thus, etiolated shoots were formed on the stored rhizome, and each shoot (length 5.6 cm, wt 7.4 g) was composed of a rhizome. The etiolated shoots and their mother rhizome were also subjected to analysis as described below.

Cultivation of the stored ginger rhizomes for the preparation of plant materials was performed as follows. The rhizome stored for five months was planted on a farm in April as propagation rhizomes to propagate fresh rhizomes. Newly propagated fresh rhizomes and their mother rhizomes were collected together with blades (mean wt/blade 1.1 g, blade number/sheath 18) and sheaths (mean length 83.6 cm, wt/sheath 45.7 g) in November. Each sheath was sepd into the greenish part (mean length 78.8 cm) and the reddish part (mean length 4.8 cm). The greenish part was further cut into upper and lower parts in equal lengths. Several groups of blades and of each part of the sheaths were separately analysed as described below.

Analysis of volatile constituents. Quintuple batches of stored rhizomes (*ca* 500 g) were first weighted and then, after being washed and cut, subjected to steam distillation. Similarly, triplicate to quintuple batches of other plant materials (*ca* 250–500 g) were subjected to steam dist. The steam dist was extd with Et_2O. The Et_2O soln, after drying (Na_2SO_4),was concd in a N_2 stream to give an essential oil. The oil was fractionated by CC on silica gel 60 (Merck) using hexane–EtOAc with EtOAc increasing from 0 to 100%. The essential oil thus obtained was analysed by a combination of GC and GC/MS. The conditions were as follows. GC: 3 m × 3 mm i.d. glass column packed with 3% OV-17 on Chromosorb W (60–80 mesh), column temp 80–250° at 2° /min; GC/MS: 3 m × 3 mm i.d. glass column packed with 3% OV-17 on Chromosorb W (60–80 mesh), column temp 80–250° at 2°/min., split ratio 120, ionization voltage 70 eV.

The data obtained were statistically treated. The mean wt of stored rhizomes and the yield and physicochemical constants of the oil from the rhizome are shown in Table 5 of the essential oils

Table 5. Weight of stored rhizomes of *Z. officinale* and yield and physicochemical constants of the essential oil from the rhizome

Storage period (month)	Relative wt	Yeild fr wt%	n_D^{25}	d_4^{25}
0	100	0.137	1.4856	0.9227
1	88.7	0.098	1.4856	0.9161
2	84.2	0.090	1.4871	0.9184
3	82.1	0.089	1.4881	0.9219
4	78.0	0.082	1.4878	0.9165
5	78.4	0.072	1.4876	0.9114
8	43.9	0.094	—	—

Table 6. Acyclic oxygenated monoterpene contents in stored rhizomes of *Z. officinale*

Storage period Month	Neral		Geraniol		Geranial		Geranyl acetate	
	%*	mg†	%*	mg†	%*	mg†	%*	mg†
0	9.7	13.3	16.1	22.1	20.0	27.4	9.7	13.3
1	11.5	10.0	9.2	8.0	27.9	24.3	3.9	3.4
2	18.1	13.7	5.0	3.8	31.7	24.0	1.1	0.8
3	21.9	16.0	3.4	2.5	35.1	25.6	1.2	0.9
4	21.1	13.5	2.1	1.3	38.5	24.6	0.4	1.3
5	20.2	11.4	3.1	1.7	35.8	20.2	0.4	0.3
8	22.9	9.4	nd	nd	37.5	15.5	nd	nd

* % of essential oil (RC).

† mg/100 g fr rhizome (AA); the AA value was calculated from the equation, $AA = RW \times Y \times RC \times 10^{-1}$, where RW and Y show the relative weight of the rhizome and the essential oil yield (Table 5), respectively. nd: not detected.

from the shoots and the cultivated ginger plant. The mean yield (dry wt %) and physicochemical constants, are as follows: shoots [1.512%]; the newly propagated rhizome [0.731%, n_D^{25} 1.4824, d_4^{25} 0.9128]; the mother rhizome [0.670%, n_D^{25} 1.4882, d_4^{25} 0.9164]; the blade [0.477%, n_D^{25} 1.4826, d_4^{25} 0.9263]; the greenish sheath, the upper part [0.376%, n_D^{25} 1.4857, d_4^{25} 0.9242]; the greenish sheath, the lower part [0.127%, n_D^{25} 1.4861]; the reddish sheath [0.916%, n_D^{25} 1.4878, d_4^{25} 0.9539]. The relative contents and absolute amounts of the acyclic oxygenated monoterpenes in the stored rhizome are shown in Table 6.

Acknowledgements—The author wishes to express her heartfelt gratitude to Prof. Takayuki Suga of Hiroshima University for his encouragement and guidance during the course of this work and his critical reading of the manuscript. Sincere thanks are also extended to President, Dr Masao Kaneda and the last President, Dr Kanzo Inoue of Oshimo Women's College for their continuous encouragement. This work was in part supported by a Grant-in-aid for No. 197 and 224 from the Foundation for In-service Training and Welfare of the Private School Personnel in Japan.

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