Phytochemistry, Vol. 24, No. 1, pp. 93–96, 1985
Printed in Great Britain

0031–9422/85 $3.00 + 0.00

THE ESSENTIAL OIL OF GREATER GALANGA (*ALPINIA GALANGA*) FROM MALAYSIA

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(*Received* 26 *April* 1984)

Key Word Index—*Alpinia galanga*; Zingiberaceae; greater galanga; aroma volatiles; chavicol acetate; GC; Kováts indices.

Abstract—The essential oil of *A. galanga*, a common spice in Malaysia, was prepared from fresh and dried rhizomes and analysed by means of capillary GC and GC/MS. Forty components were identified (only three of which were previously reported), accounting for 83–93% of the oil, depending on its method of preparation. Apart from monoterpenes, monoterpene alcohols and esters, and sesquiterpenes, also methyleugenol, eugenol acetate, chavicol (4-allylphenol) and chavicol acetate were present. This is the first time the latter substance has been reported in nature. Standardization of GC is proposed and tentatively applied towards a more systematic use of the Kováts indices as an aid in the identification of the constituents of essential oils.

INTRODUCTION

Greater galanga (*Alpinia galanga* Willd. or *Languas galanga* Stuntz, according to Burkill [1]) is cultivated throughout Malaysia, and the rhizomes are sold as such on the market for use in the preparation of meat dishes and curries, or are dried in the sun and then milled into a powder, which is used for flavouring foods. Whereas the oil of lesser or smaller galanga (*Alpinia officinarum* Hance), which is cultivated in China and mainly used as a drug, has been thoroughly studied [2], little information is available in the literature about the steam volatile oil of greater galanga. According to Guenther [3], steam distillation of fresh rhizomes yields 0.04% of oil. An optical rotation of +4° 20′ and an ester number of 145.6 were recorded for a sample from Java [4]. Studying an analogous oil, Ultée [5] reported the presence of (+)-pinene (probable), 1,8-cineole (20–30%), camphor and methyl cinnamate (48%). On repeating the analysis with an Indian oil (yield 0.25%), Nigam and Radhakrishnan found an optical rotation of −3° 27′ and a much lower ester value (saponification value = 49.4). Their sample contained 1,8-cineole (5.6%), methyl cinnamate (2.6%) and a large number of unidentified sesquiterpenes. No camphor or pinenes were detected [6, 7].

There is no agreement on the description of the odour of the different oil samples of greater galanga. It is alternatively described as "strong spicy, peculiar" [4], "camphorous, cineole-like" [5] or "aromatic, pleasant" and quite different from that of lesser galanga [8].

RESULTS AND DISCUSSION

The essential oil was prepared in a low yield (0.04–0.15%) by steam distillation of fresh, comminuted rhizomes and collected on top of the distillate. It was greenish-yellow to yellowish-brown and had the following physical properties (28°): specific gravity 0.9810, refractive index 1.4780 and optical rotation +4° 30′ (Table 1, A). Alternatively, the essential oil was isolated by extraction of the steam distillate with dichloromethane (Table 1, B). In a third preparation, dried, finely milled rhizomes were submitted to steam distillation and the oil was extracted with dichloromethane (yield 0.4%) (Table 1, C).

No unequivocal description of the aroma of the different oils can be given as it is quite dependent on the method of preparation. When obtained from fresh rhizomes and recovered directly (A), the oil has a pleasant, very weakly camphoraceous, floral, spicy smell. When obtained by extraction of the steam distillates (B and C), the first impression is strongly camphoraceous–spicy, which turns into floral–spicy a short while after application of the oil on a paper wick. The reason for this behaviour is revealed by gas chromatography, because in oil A (Table 1) the major components (α-pinene, 1,8-cineole, bornyl acetate, geranyl acetate, α-bergamotene, *trans*-β-farnesene and β-bisabolene) are relatively equally distributed, and mostly impart camphoraceous, floral, fruity or spicy notes to the aroma, which corresponds to the general olfactive evaluation of the oil. On the other hand, oils B and C (Table 1) show a higher 1,8-cineole content, which overrides the other odours.

For the identification of the different components, GC and GC/MS on capillary OV-1 columns of the oil as such, and after its fractionation on a preparative Carbowax 20 M column, were originally thought to be amply sufficient. However, this was found to be too optimistic a notion in connection with the sesquiterpenes. It became obvious that identifications based solely on the comparison of mass spectra with published ones might lead to erroneous conclusions owing to variations in published spectra; to the similarity in the spectra of different substances; and to the dependence of spectra on the mode of recording (direct or after GC/MS). An important aid in the identification would have been the retention in GC

Table 1. Composition (in %) of the essential oil of greater galanga prepared by different methods. (A) Fresh rhizomes, oil recovered on top of the steam distillate, (B) fresh rhizomes, extraction of the steam distillate; (C) finely milled, dried rhizomes, extraction of the steam distillate

Compound	Kováts indices on OV-1		A	B	C	Odour
	column 1	column 2				
2-Methylpropyl acetate	754	754		0.2		Fruity
Butyl acetate	799	797		0.9		Fruity
α-Pinene	926	928	10.2	0.8	0.2	Turpentine
Camphene	937	941	0.5	tr		
Sabinene	960	966	tr	tr		
β-Pinene	963	968	1 6	0.1	0 3	Turpentine
Myrcene	980	981	0.7	0 2	0.4	Acidic, weakly lemon-like
p-Cymene	1008	1012	0.8	0 2		Weakly lemon-like
1,8-Cineole	1015	1019	5 5			Cool, camphoraceous
				58 5*	24.0*	
Limonene	1017	1021	1.6			Lemon-like
γ-Terpinene	1044	1048	tr	0.1		Lemon-like
Terpinolene	1075	1078	tr	tr		
Linalool	1085	1085	tr	0 3		Floral
Unidentified $[M]^+$ at *m/z* 134	1102	1104	tr	0.2		Soapy
Unidentified $[M]^+$ at *m/z* 134	1119	1121		0 1		Soapy
Unidentified $[M]^+$ at *m/z* 136		1132	0 2	tr		
Borneol	1144	1149	tr	0 5	0.3	Camphoraceous
4-Terpineol	1155	1162	0.3	2.2	7.0	Lemon-like
p-Cymenol	1159	1162	tr	tr	tr	
α-Terpineol	1169	1174	0.2	2.2	0.8	Weakly lemon-like
Unidentified	1179	1182	tr	0.2	0.1	
Carveol I	1196	1202		tr		
Carveol II	1208	1217		tr		
Chavicol	1243	1249	0.2	tr		Camphoraceous
Bornyl acetate	1264	1269	2.5	0.7	0.2	Fresh-piney
Tridecane	1300	1300	tr	tr		
Chavicol acetate	1309	1314	1.0	0.5	2.8	Weakly spearmint-like
Unidentified	1321	1320	0.1	tr		
Citronellyl acetate	1336	1334	1.6	0.4		Fruity-floral
Neryl acetate	1342	1341		tr		
Unidentified	1351	1346		0.2		Spicy
Geranyl acetate	1361	1361	5 1	1.4	0 9	Fruity-floral
α-Copaene	1363	1373	0.7	3.6	1.4	Floral
Methyleugenol	1368	1373				
Branched C_{14}-hydrocarbon	1378	1384	0.4	tr		
β-Caryophyllene	1403	1414	0.9	0.5	1.8	Spicy-piney
α-Bergamotene	1425	1432	10.7	1.7	0.9	Spicy-sweetish
α-Humulene	1436	1445	0.6			
trans-β-Farnesene	1444	1447	18.2	8 1	30.6	Pleasant, very weakly floral
Santalene (?)		1452	0 8			
ar-Curcumene	1463	1468	1 9	0.3	0 6	Spicy
Unidentified $[M]^+$ at *m/z* 204	1475	1471	0 8	tr		
Eugenyl acetate	1483	1482	1 5	2.3	2.7	Clove oil
Unidentified $[M]^+$ at *m/z* 210 $C_{15}H_{30}$		1485	0.1	0.2	4 7	Incense-like
β-Bisabolene	1493	1503	16.2	3.9	4.9	Pleasant, weakly fruity
Pentadecane	1500	1500	1 9			
β-Sesquiphellandrene	1507	1512	1 6	3 2	2.2	Weakly spicy
Unidentified $[M]^+$ at *m/z* 204	1512	1521		1 3	1 5	Musty, woody
Caryophyllene oxide	1553	1571	2 5			Floral

*Unresolved peaks, mainly containing 1,8-cineole.

tr = trace, < 0.1 %

columns as expressed by the Kováts indices [9, 10], but although an impressive amount of essential oils have been analysed, relatively few authors have recorded these values. Moreover, the total lack of standardization (mainly because of the multitude of available stationary phases) makes the situation even worse. A case in point is the analysis of ginger oil (composed almost exclusively of ar-curcumene, zingiberene, β-bisabolene and β-sesquiphellandrene, which were needed for the conclusive identification of the corresponding substances in Table 1) for which varying elution times and elution sequences of the compounds (up to complete reversal) are given [10–16].

A supplementary difficulty arose when it was observed that Kováts indices sometimes changed slightly in the normal life span of the OV-1 columns (e.g. for β-caryophyllene, from 1415 to 1403). A method was then sought which would stabilize the column. It was found that when OV-1 capillary columns, freshly prepared by the static method [17], were treated with hexamethyldisilazane, two kinds of stable GC analyses for β-caryophyllene were obtained: on column 1 (Table 1), Kováts index 1403–1404 and on column 2, 1414–1415. Subsequently, the use of these columns allowed fast preliminary identification of the composition of a series of essential oils.

To ascertain the identities of ar-curcumene, zingiberene, β-bisabolene, β-sesquiphellandrene and β-caryophyllene and α-humulene, these compounds were isolated from ginger oil (β-bisabolene in extremely low yield) and clove oil, respectively, and purified. A number of unknowns, with Kováts indices larger than 1550, consisting mainly of sesquiterpene alcohols (as deduced from their removal by liquid chromatography on Al_2O_3 columns, and from their mass spectra), imparted weak, spicy, woody or floral notes to the oil.

On comparison of the composition of the oil of greater galanga of Malay origin with the results of earlier workers [5–7], only the presence of pinenes and 1,8-cineole was confirmed, but no camphor or methyl cinnamate was detected. An analogous observation was made by Lawrence *et al.* [2] who investigated the oil of lesser galanga (*Alpinia officinarum* Hance) very thoroughly, and could not detect methyl cinnamate, although an earlier report [18] included the substance among the constituents of the oil. It was argued that the absence of a component in a plant of a genus might be due to differences in the growing conditions, or to the method of preparation of the oil. However, the results of the present investigation and those of Lawrence *et al.* [2], Purohit and Devi (about *A. allughas* containing no methyl cinnamate) [19], and Goutam and Purohit (about *A. khulanjan* having a high methyl cinnamate content) [20] tend to shed doubt on the assumption that the ester has a chemotaxonomic value for *Alpinia*, and this might warrant further investigation of other species.

At the moment, a distinguishing feature of the galanga oil of Malay origin seems to be the presence of relatively large amounts (up to 2.8%) of chavicol acetate (4-allylphenol acetate), the structure of which was confirmed by synthesis. Whereas chavicol (4-allylphenol) has been found in nature (e.g. refs. [21–23], tentatively in ginger [24]), there are no reports in the literature on the natural occurrence of its acetate.

EXPERIMENTAL

Rhizomes of greater galanga were purchased locally in Kuala Lumpur, Malaysia.

Analytical GC. Solutions of 1–5 μl oil in 250 μl CS_2 were analysed by injection of the sample (1 μl) into Varian model 2700 or 3700 instruments, equipped with a glass capillary column (i.d. 0.5 mm; length: 30, 36, 60 m; coated with OV-1, thickness 0.8 μm) and a FID. Working conditions: injector and detector temps. 210° and 250°, respectively; oven temp. programmed from 40° to 220° at 2°/min; carrier gas 4 ml He/min. Peak areas were calculated by a PDP 11/34 computer. For reference purposes, Kováts indices were obtained from the temp. programmed GC, using the homologous series of C_6–C_{18} *n*-alkanes as standards, by linear interpolation [9]. Before use, the OV-1 columns were treated with hexamethyldisilazane in batches of 1 μl at 150° until the Kováts indices of 1,8-cineole, limonene, β-caryophyllene and α-humulene remained stable at 1014–1015, 1017–1018, 1403–1404 and 1435–1436 (column 1; Table 1), or at 1019–1020, 1021–1022, 1414–1415 and 1444–1445, respectively (column 2, Table 1).

GC/MS A Varian model 2700 gas chromatograph equipped with a glass capillary column (60 m, OV-1) was connected directly by way of a splitter and a platinum capillary (at 220°) to the ion source of a Varian Mat 112 mass spectrometer Working conditions: GC as above; MS: ion source 250°, 70 eV; electron current 300 μA. Mass spectral identifications were based on published spectra [12, 25–28], followed by comparison of the spectra and Kováts indices with those of reference compounds, which were purchased, synthesized or isolated from, or identified in, essential oils of known composition.

Preparative GC was performed in a Varian 1700 instrument equipped with a catharometer and a 3 m glass column (i.d 4 mm) packed with 10% Carbowax 20 M (or 15% Apiezon L) on Chromosorb W-AW. Working conditions: injector and detector temps. 210°; oven temp. 160°; carrier gas 25 ml H_2/min. Samples of 25 μl oil B (see Table 1) were repeatedly injected on the Carbowax column and each time 9 fractions were collected at the outlet of the instrument in ice-cooled U-tubes (total length 20 cm). The condensed material was removed from the tubes with 1 ml CH_2Cl_2. Each fraction was then separately analysed on a capillary OV-1 column by GC/MS.

Reference compounds. A crude mixture of β-caryophyllene and α-humulene, obtained by stripping clove oil of eugenol and eugenol acetate by hydrolysis and extraction with alkali, was separated by prep. GC on a packed Apiezon-L column (see above).

β-Farnesene was synthesized according to ref. [29] in low yield and purified by prep. GC as above.

Zingiberene, ar-curcumene, β-bisabolene and β-sesquiphellandrene were obtained from ginger oil, which was first freed from polar compounds by Al_2O_3 column chromatography. The resulting terpene fraction was then crudely separated according to unsaturation by LC through an Al_2O_3–20% $AgNO_3$ column [2, 30] using as eluants *n*-hexane (yielding crude ar-curcumene), Et_2O (yielding a crude mixture of zingiberene and β-sesquiphellandrene) and Me_2CO (yielding crude β-bisabolene) The sesquiterpenes were separated further and purified by repetitive prep. GC on the Apiezon L column. The structure assignments of all the above sesquiterpenes were confirmed by their IR spectra [31]. α-Bergamotene was identified by comparison with the corresponding component of bergamot oil.

Methyleugenol was prepared by methylation of eugenol with (Me_2SO_4 in DMF–K_2CO_3, according to ref. [32]. A commercial mixture of neral and geranial was reduced to nerol and geraniol, acetylation of which yielded a mixture of the acetates

Chavicol (4-allylphenol) was synthesized starting from 4-bromophenol, which was first transformed into the tetrahydropyranyl ether. Subsequent treatment with Mg in tetrahydrofuran

yielded the organomagnesium derivative. Alkylation was then performed by reaction of the latter substance with allyl bromide, after which chavicol was set free by hydrolysis in dilute HOAc. The method is analogous to that of Kitamura *et al.* [33], but instead of using chloromethyl methyl ether (a suspected carcinogen) as a protecting agent, dihydropyran was employed. Acetylation into chavicol acetate was performed in the usual way. Mass spectrum by GC/MS: *m/z* (rel. int.): 176 $[M]^+$ (14) 134 (100), 133 (80), 43 (40), 107 (25), 77 (17), 105 (14), 135 (14), 176 (14), 91 (10), 117 (10).

Odour assessment. The components of the essential oil were separated in a capillary OV-1 column in a Varian 2700 gas chromatograph as described above. The instrument was equipped with a splitter leading 1/5 of the eluant to a FID and 4/5 through a capillary (i.d. 0.5 mm) to the outside, where the odour of the eluting substances was assessed by sniffing. For confirmation, the same analysis was performed with reference compounds and essential oils of known composition.

Acknowledgements—The Nationaal Fonds voor Wetenschappelijk Onderzoek, the Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw and the Ministerie voor Wetenschapsbeleid are thanked for their financial aid. One of us (M.N.O.) thanks the World Bank for financial support, making his 2-month stay in the State University of Gent, Belgium, possible.

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