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ANALYSIS OF THE VOLATILE ESSENTIAL OILS OF *MURRAYA KOENIGII* AND *PANDANUS LATIFOLIUS*

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Key Word Index—*Murraya koenigii*; Rutaceae; *Pandanus latifolius*; Pandanaceae; curry leaves; essential oils.

Abstract—Using well-established techniques, samples were obtained of the volatile essential oils of the two types of curry leaf, *Murraya koenigii* and *Pandanus latifolius.* Both contained mainly terpenes, and *M. koenigii* produced less than 4% of other components with eight monoterpene hydrocarbons (*ca* 16%) and 17 sesquiterpene hydrocarbons (*ca* 80%) being obtained. The most important constituents of *M. koenigii* are β-caryophyllene, β-gurjunene, β-elemene, β-phellandrene and β-thujene. The volatile essential oil of *P. latifolius* also contained mainly sesquiterpene hydrocarbons (6–42%) but the only monoterpene was linalool (*ca* 6%). Nearly 2000 times the total quantity of aroma volatiles was produced by *M. koenigii* compared with *P. latifolius*, and this partly explains the observed stronger flavour potency of the former.

INTRODUCTION

One of the most widely used plants whose leaves are added to curries to improve flavour is the small tree, *Murraya koenigii* Spreng. The intensely pungent, aromatic leaves are best when fresh, but adequately retain their potency for some time after picking. A number of studies concerning the composition and qualities of *M. koenigii* leaves have been carried out, mainly by Indian workers, and in particular Mitra has shown that steam distillation yields *ca* 2.6% of essential oil [1], and Prakash and Natarajan obtained indications of the presence of caryophyllene, α-pinene and β-pinene in the volatile oil [2]. The leaves of *Pandanus latifolius* Sol. are also commonly added to curries to increase flavour, but they are less extensively used than *M. koenigii*, probably due to their less intense aroma. Although the leaves of both these plants are widely used for flavouring curries there has been no detailed study of the nature of their volatile aroma components. This paper describes the analysis of the concentrated essences of these two types of curry leaf.

RESULTS AND DISCUSSION

Essences possessing the concentrated aromas of the two types of curry leaf were obtained by well-established procedures [3–6]. The best extracting solvent of those tested for these leaves was trichlorofluoromethane, and its advantages in this type of work have been described [3]. The essences were examined by routine temperature programmed GC and constituents were identified as far as possible by high sensitivity GC/MS using electron impact ionization and chemical ionization techniques.

Table 1 details the results obtained for the analysis of the volatile essential oil of the curry leaf *M. koenigii* and Table 2 lists similar data for *Pandanus latifolius.* Where positive identities are given, mass spectra of sample components agreed well with those in the literature [7–10] within instrumental variability. However, since many components were mono- or sesquiterpenes and since spectra of such compounds can be confusing due to their great similarity (e.g. the spectra of certain sesquiterpene hydrocarbons) summaries of the mass spectra of some of the more interesting terpenes identified in this work are given in Table 3. Literature [8, 11] Kováts retention indices of most of these components (determined on the same phase as employed in this project) are included in Tables 1 and 2, and these serve as limited supportive evidence of identity.

From the results of the analysis of the leaves of *M. koenigii* (Table 1), it can be seen that the essence contained 48 main components of which 27 (comprising *ca* 83% of the sample) have been positively identified, with a further nine (*ca* 14%) partially characterized. Only six components (*ca* 0.7%) remained unidentified, the remainder of the sample being made up of six late-eluting GC peaks referred to as 'hydrocarbons'. Whilst these compounds may well have been genuine hydrocarbons, it should be emphasized that their mass spectra exhibited only typical alkyl fragments and no molecular ion peaks. It is possible, therefore, that these components may have contained long alkyl fragments attached to some

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Table 1. Volatile flavour components of *Murraya koenigii*

Peak no.	Component	R_t (min)	Kováts index (literature)*	% rel. abundance	μg/kg fr. leaf
1	Unknown	0.3	—	<0.1	3.5
2	Trichlorofluoromethane	0.9	—	<0.01	0.4
3	Hexa-2, 4-diene	1.4	—	0.1	5.4
4	Carbon tetrachloride	2.7	—	<0.01	0.5
5	2-Methylbutanal	3.5	—	0.1	12.1
6	Dichloromethane	4.4	—	<0.1	1.1
7	Unknown	5.4	—	<0.1	1.8
8	β-Thujene	7.6	—	4.3	380.7
9	Dimethyl disulphide plus camphene	10.5	1081 1083	<0.1	4.1
10	β-Pinene	11.7	1124	0.7	66.1
11	*m*- and/or *p*-xylene	12.6	1145	tr	tr
12	α-Phellandrene	13.1	1177	0.6	52.3
13	Pyridine	13.7	1180	0.1	9.0
14	Limonene	13.9	1206	2.1	188.2
15	β-Phellandrene	14.2	1216	6.1	545.7
16	*trans*-β-Ocimine	14.5	1250	1.9	168.8
17	*p*-Cymene	14.9	1272	0.1	8.2
18	Unknown	15.2	—	<0.1	3.8
19	*cis*-Hex-3-en-1-yl acetate	15.7	1300	<0.1	2.2
20	Unknown	16.3	—	<0.1	1.1
21	*cis*-Linalool oxide	16.8	1423	<0.1	2.8
22	α-Cubebene	17.1	—	0.2	17.3
23	α-Copaene	17.5	1520	0.9	76.6
24	A selinene	17.9	—	0.2	14.2
25	β-Elemene	18.4	—	6.8	607.3
26	β-Caryophyllene	18.8	1618	28.7	2563.2
27	β-Gurjunene	19.5	—	21.4	1908.1
28	A selinene	20.1	—	4.3	381.6
29	Sesquiterpene hydrocarbon	21.5	—	0.3	24.4
30	ϵ-Muurolene	22.2	—	0.4	36.0
31	Sesquiterpene hydrocarbon	23.4	—	0.4	33.0
32	β-Bisabolene	24.9	1726	2.8	251.5
33	γ-Cadinene	26.8	1762	2.5	224.5
34	Unknown	28.1	—	<0.1	4.5
35	α-Selinene	29.0	—	2.9	262.4
36	? Guaiene	30.6	—	0.4	33.0
37	Sesquiterpene hydrocarbon	31.6	—	<0.01	0.6
38	Sesquiterpene hydrocarbon	32.6	—	<0.01	0.5
39	A selinene	34.0	—	8.2	726.6
40	Terpene	36.1	—	0.4	39.4
41	Hydrocarbon	38.8	—	0.1	9.9
42	Hydrocarbon	41.1	—	0.2	16.7
43	Hydrocarbon	44.1	—	<0.01	0.1
44	Unknown	46.2	—	0.6	49.5
45	Hydrocarbon	50.7	—	0.1	9.7
46	Hydrocarbon	57.7	—	0.2	16.2
47	Hydrocarbon	68.8	—	1.7	153.4

*Literature = [8, 11], tr = trace.

other group or nucleus, although none was evident in the spectra. Most of the components of the essence were terpenes, consisting of eight monoterpene hydrocarbons (15.9%) and 17 sesquiterpene hydrocarbons (80.2%). Indeed, other identified constituents represented less than 1% of the sample. Thus the intense, characteristic aroma of *M. koenigii* is probably due entirely to terpene hydrocarbons, and presumably the major components (β-caryophyllene, β-gurjunene, β-elemene and β-phellandrene) are the most important aroma constituents. Whilst it was possible completely to characterize the monoterpenes from their mass spectra, a number of the sesquiterpenes could be identified only tentatively. Thus four selinenes were recognized (*ca* 16%), but only one could be fully characterized. All of the identified terpenes have been located previously in aroma volatiles of various foods, so none would appear to be

Table 2. Volatile flavour components of *Pandanus latifolius*

Peak no.	Component	R_t (min)	Kováts index (literature)*	% rel. abundance	μg/kg fr. leaf
1	Unknown	1.4	—	tr	tr
2	Unknown	2.7	—	0.2	0.01
3	Dimethyl sulphide	3.2	—	0.2	0.01
4	C_8 branched chain hydrocarbon	4.3	—	0.2	0.01
5	Acetone	4.9	810	2.7	0.14
6	Unknown	6.3	—	tr	tr
7	Carbon tetrachloride	6.7	—	2.4	0.12
8	Unknown	7.2	—	0.3	0.01
9	2-Methylbutanal	7.7	—	0.2	0.01
10	Unknown	8.1	—	tr	tr
11	Diacetyl	8.5	963	0.7	0.04
12	Unknown	8.9	—	0.6	0.03
13	Unknown	9.2	—	0.2	0.01
14	3-Methylbut-3-en-2-one	9.5	—	2.0	0.10
15	Chloroform	10.0	—	2.4	0.12
16	Unknown	10.4	—	tr	tr
17	Unknown	10.8	—	0.3	0.02
18	Toluene	11.1	—	1.0	0.05
19	Unknown	11.6	—	0.4	0.02
20	Unknown	11.9	—	tr	tr
21	Unknown	12.2	—	tr	tr
22	Pent-3-en-2-one	12.5	—	1.1	0.05
23	Unknown	12.8	—	tr	tr
24	3-Methylbutan-1-ol	13.3	1184	2.1	0.10
25	Pyridine	13.9	1180	0.7	0.03
26	Unknown	14.3	—	tr	tr
27	Pentylfuran	14.6	1229	1.0	0.05
28	Unknown	14.9	—	tr	tr
29	Unknown	15.2	—	tr	tr
30	Styrene	15.7	—	12.1	0.62
31	Hexan-1-ol	16.7	1316	1.0	0.05
32	Unknown	17.2	—	0.4	0.02
33	? Formylthiophen	17.9	—	14.9	0.76
34	Unknown	19.5	—	tr	tr
35	Unknown	19.9	—	0.2	0.01
36	Unknown	22.5	—	0.2	0.01
37	Linalool	23.4	1506	5.7	0.29
38	Sesquiterpene hydrocarbon	24.9	—	2.6	0.13
39	Unknown	27.0	—	0.3	0.01
40	Unknown	28.0	—	0.2	0.01
41	? Isocaryophyllene	28.7	—	tr	tr
42	β-Caryophyllene	29.6	1618	10.8	0.55
43	β-Farnesene	31.6	1630	3.6	0.18
44	Unknown	34.6	—	0.3	0.01
45	1, 2-Dimethoxybenzene	36.3	—	2.9	0.15
46	α-Humulene	37.1	1682	0.8	0.04
47	β-Selinene	42.1	1730	24.3	1.24
48	Unknown	44.6	—	0.2	0.01

*Literature = [8, 11], tr = trace.

particularly characteristic of *Murraya*. However, β-gurjunene (21.4%) and β-thujene (4.3%) seem to be much less common than most of the others, and so may be particular contributors to the unique aroma.

Table 2 lists the 48 main components which were detected in the essence from *P. latifolius* leaves. Of these, 20 (*ca* 78% of the sample) were positively identified and four (*ca* 18%) were tentatively identified. The 24 unknown components represented less than 5% of the sample. Again, sesquiterpene hydrocarbons provided the major fraction (6–42%), but in *Pandanus* no monoterpene hydrocarbons were detected, although linalool was present to the extent of 5.7%. Presumably the sesquiterpenes are major contributors to the aroma of this curry leaf, particularly β-selinene and β-caryophyllene, but other compounds such as styrene (*ca* 12%) and the tentatively identified formylthiophen (*ca* 15%) may be

Table 3. Summaries of mass spectra of some monoterpene and sesquiterpene hydrocarbons identified in *Murraya koenigii* and *Pandanus latifolius*

β-Thujene	*m/z*	93	121	68	79	77	91	136	92	67	105	107	80	
	% rel.int.	100	52	46	45	40	38	35	32	32	28	22	20	
Camphene	*m/z*	93	121	79	67	77	68	91	107	136				
	% rel.int.	100	58	40	38	30	28	27	25	20				
α-Phellandrene	*m/z*	93	77	91	92	79	119	136	94	121	80			
	% rel.int.	100	28	26	19	16	15	15	13	10	8			
β-Phellandrene	*m/z*	93	136	77	91	79	94	80	92	121				
	% rel.int.	100	35	25	22	19	15	12	10	9				
trans-β-Ocimene	*m/z*	93	80	79	77	92	91	121	105	136	107			
	% rel.int.	100	45	40	32	30	28	25	21	20	10			
α-Cubebene	*m/z*	161	119	105	81	91	204	41	93	121	95			
	% rel.int.	100	85	65	48	45	41	40	35	28	25			
α-Copaene	*m/z*	161	105	119	93	204	41	91	92	77	81	55	79	
	% rel.int.	100	85	83	73	60	55	40	35	31	25	20	16	
β-Elemene	*m/z*	93	41	68	81	55	107	91	79	77	121	161	204	147
	% rel.int.	100	95	86	85	71	60	50	46	43	35	29	25	21
β-Farnesene	*m/z*	41	69	93	79	55	133	81	67	105	133	161	107	204
	% rel.int.	100	95	90	47	45	41	40	37	25	21	20	20	18
β-Gurjunene	*m/z*	41	161	93	91	107	105	79	55	77	80	121	147	204
	% rel.int.	100	90	81	78	65	60	44	40	38	35	30	15	12
ϵ-Muurolene	*m/z*	161	91	105	119	41	55	81	145	204				
	% rel.int.	100	82	79	75	58	43	32	30	18				
α-Humulene	*m/z*	93	80	41	121	79	91	107	105	204	53	67	136	
	% rel.int.	100	43	40	30	28	26	25	23	20	18	15	10	
β-Bisabolene	*m/z*	69	41	93	79	81	107	55	95	91	109	119	204	161
	% rel.int.	100	95	72	59	51	50	46	44	36	35	31	30	18
β-Selinene	*m/z*	41	204	93	107	81	105	55	67	79	121	189	161	
	% rel.int.	100	98	52	49	42	40	38	38	36	25	25	24	
γ-Cadinene	*m/z*	161	204	41	91	79	105	93	56	81	77	69	95	
	% rel.int.	100	45	42	40	32	30	30	28	25	22	18	15	
α-Selinene	*m/z*	41	55	204	93	81	189	80	107	91	67	161	105	133
	% rel.int.	100	68	65	63	61	59	55	54	47	44	35	24	22

important, as well as linalool. An interesting identification was that of 1,2-dimethoxybenzene which is rare as an aroma volatile of foods. Most of the other identified components are relatively common aroma volatiles, so would not appear to be characteristic of *Pandanus*. However, β-selinene (24.3%) and β-farnesene (3.6%) are more unusual constituents and β-selinene in particular may be an important aroma volatile.

The quantitative data given in Tables 1 and 2 show that in total only *ca* 5 μg of aroma components were obtained per kg fresh *P. latifolius* leaf, whilst the corresponding figure for *M. koenigii* was *ca* 9 μg/g. Thus the latter yielded nearly 2000 times the concentration of aroma volatiles of the former. These figures partly explain why the aroma intensity of the leaves of *M. koenigii* is so much greater than that of *P. latifolius* leaves, but they do not, of course, take into account differences in odour potencies of the constituents of the two systems. However, considering the compounds identified in the two leaves, it seems unlikely that variations in odour thresholds would compensate for the considerable difference in absolute concentration of volatiles. It is noticeable also that *Pandanus* appears to produce quite large percentages of some relatively insignificant, but sometimes interesting, volatiles, such as acetone, carbon tetrachloride, chloroform, 3-methylbutan-1-ol, etc., whilst these or similar compounds were not generally produced by *Murraya*. None of these compounds was a contaminant from the solvent, but some conceivably could be pesticide residues. However, whilst *Murraya* liberated 0.5 μg/kg of carbon tetrachloride, for example, *Pandanus* gave only 0.12 μg/kg, representing 2.4% of the aroma volatiles against less than 0.01% in the former (due to the difference in total absolute concentration). Thus many of these volatiles may have been submerged in the more concentrated *Murraya* essence.

EXPERIMENTAL

Leaves of *M. koenigii* and *P. latifolius* were picked from trees in Colombo, Sri Lanka, and were transported by air to London for analysis the following day.

Sample preparation. Leaves (100 g) were chopped, mixed with H_2O (500 ml) and extracted for 4 hr in a Likens and Nickerson apparatus [5], as modified by MacLeod and Cave [6] using trichlorofluoromethane (20 ml) as solvent. Extracts were concd to 1.0 ml by low temp.—high vacuum distillation [6].

Gas chromatography. Samples were analysed by routine temp. programmed GC (60° for 5 min, followed by an increase at 16°/min to 195°) with heated FID and a 5.5 m × 4 mm i.d. glass column packed with 10% Carbowax 20 M coated on 100–120 BSS mesh acid-washed Diatomite C.

Gas chromatography/mass spectrometry. Constituents of the essences were identified by GC/MS. Both EI- and CI-MS were performed.

Quantitative assessment. Samples were prepared in such a manner that known aliquots of leaf samples were analysed. Quantitative data were then derived both from the traces obtained from the TIC monitor during GC/MS and from the FID traces during routine GC. Known amounts of a selection of identified compounds (2-methylbutanal, 3-methylbutan-1-ol, limonene, *cis*-hex-3-en-1-yl acetate and hexan-1-ol) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the essences.

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