THE ESSENTIAL OILS OF *CLAUSENA LANSIUM*

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IBRAHIM JANTAN, NOR AZAH MOHD ALI & RASADAH MAT ALI. 1993. The essential oils of *Clausena lansium*. Water distillation of the leaf and wood of *Clausena lansium* yielded 0.05% and 1.60% of essential oils respectively. The essential oils were analysed by means of gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). The leaf oil was almost entirely made up of sesquiterpenoids of which δ-cadinene (47.2%) and ß-bisabolene (20.0%) were the major components. The wood oil consisted mainly of monoterpenes (more than 70% of the oil) of which B-phellandrene (55.0%) was the most abundant component.

Key words: *Clausena lansium*-gas chromatography-sesquiterpenoids-monoterpenoids - δ-cadinene - ß-bisabolene - ß-phellandrene

IBRAHIM JANTAN, NOR AZAH MOHD ALI & RASADAH MAT ALI. 1993. Minyak pati *Clausena lansium*. Penyulingan hidro ke atas daun dan kayu *Clausena lansium* telah menghasilkan 0.05% dan 1.60% minyak pati masing-masing. Minyak pati tersebut dianalisa dengan menggunakan kromatografi gas (KG) dan gabungan kromatografi/spektromeri jisim (KG/SJ). Hampir keseluruhan minyak pati terdiri daripada seskuiterpena, dimana δ-cadinena (47.2%) dan ß-bisabolena (20.0%) merupakan komponen-komponen utama. Minyak pati dari kayu kebanyakkannya mengandungi monoterpena yang merangkumi lebih 70% daripada minyak tersebut, dimana ß-felandrena (55.0%) merupakan komponen yang terbanyak.

Introduction

Clausena lansium (Rutaceae) known locally as 'whampi' is a cultivated fruit tree, grown by the Chinese mainly for its small resinous lime fruits. The 'whampi' leaves are said to be used traditionally in hairwash against dandruff. The immature fruits are used by the Chinese to treat bronchitis (Burkill 1966). In the southern part of China and in Taiwan, the leaves are used as a folk medicine for the treatment of coughs, asthma and gastro-intestinal diseases, while the fruits and the seeds are used for digestive disorders and gastro-intestinal diseases respectively (Kan 1972).

The extracts of aerial and underground parts of *C. lansium* have been studied for the presence of new constituents. The most common compounds isolated from the leaf and seed extracts are found to be amide derivatives (Yang *et al.* 1988, Lin 1989). Another new compound isolated from the aerial parts of the species is a triterpene alcohol, lansiol (Lakshmi & Kapil 1989). Lactones are present in the bark (Khan *et al.* 1983, Kong *et al.* 1983). Khan *et al.* (1983) isolated a new furocoumarin, wampetin, from the root bark of *C. lansium.* However, the volatile constituents of this species have not been thoroughly

investigated. The present paper reports on the chemical constituents of the leaf and wood oils of *C. lansium.*

Material and methods

Collection of materials

Fresh leaves and wood of *Clausena lansium* were collected at the Forest Research Institute Malaysia, Kepong (FRIM). The plant materials were air dried under shade at room temperature for two days. The sample was identified at the herbarium of FRIM.

Chemical analysis of the essential oils

The ground samples (200 *mg*) (mesh size 40-60) were hydrodistilled in a Clavenger apparatus for 6*h*. The oily layer (after removal of excess water) was further dried by anhydrous sodium sulphate. The aqueous layer from the distillate was extracted with diethyl ether. The ether layer was dehydrated with anhydrous sodium sulphate and the solvent was distilled at slightly reduced pressure to recover the dissolved oil. The yields were averaged over two experiments and calculated based on the dry weights of the plant materials.

The oils were examined by a GLC Shimadzu GC 9A gas chromatograph equipped with FID detector using SE 30 and PEG 20M stationary phase capillary columns (25 × 0.25 *mm* i.d.) and nitrogen as carrier gas at a flow rate of 50 cm^3 min^{-1}. The gas chromatograph was programmed initially at 60°*C* for 10 *min*, then 3°C min^{-1} to 180°*C*. The oils were also analysed by GLC-MS with a Hewlett Packard GCMSD 5890 series 2 mass spectrometer from a Silicon OV 1 capillary column (12 × 0.2 *mm* i.d.) initially at 60°*C* for 10 *min*, then programmed at 3°*C* min^{-1} to 180°*C* for 1 *min* with helium as the carrier gas.

Kovat indices were obtained from the gas chromatogram by logarithmic interpolation between bracketing alkanes. The homologous series of C_9 - C_{20} n-alkanes were used as standards (Kovats 1965). The compounds were tentatively identified by comparison of their retention times and mass spectra with those of authentic specimens.

Results and discussion

The leaf oil of Clausena lansium

Water distillation of the leaf of *C. lansium* yielded 0.05% of a colourless oil with a strong spicy odour. Gas chromatographic analysis of the leaf oil resolved it into at least 30 compounds of which 12 were identified by comparing their mass fragmentation patterns with the data available in the literature and co-injection with authentic samples on columns of different polarity. The identified compounds which accounted for 76.6% of the oil were sesquiterpenoids hydrocarbons

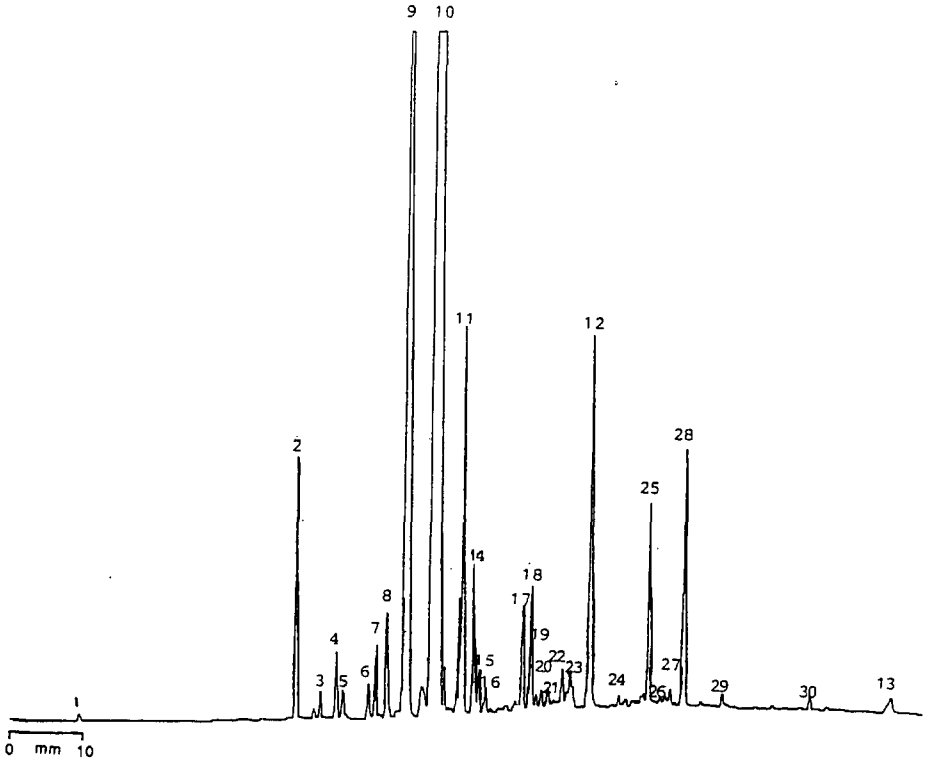

Figure 1. Gas chromatogram obtained with capillary SE 30 column for the leaf oil of *Clausena lansium;* for identity of peaks, see Table 1

Table 1. Composition of the leaf oil of *Clausena lansium* (column: 25 *mm* SE 30)

Peak number	Compound	Retention indices (*KI)	%	Identified by
1	4-methylacetophenone	1200	0.2	a
2	β-caryophyllene	1422	2.6	a & b
3	$C_{15}H_{24}$	-	0.3	a
4	elemene [i]	1430	1.3	a
5	α-bergamotene	1438	0.3	a
6	α-humulene	1456	0.5	a & b
7	β-farnesene [i]	1478	0.6	a & b
8	γ-elemene [i]	1492	0.7	a
9	β-bisabolene	1502	20.0	a
10	δ-cadinene	1527	47.2	a
11	nerolidol [i]	1550	4.7	a & b
12	β-sinensal [t]	1620	1.6	a
13	phytol	2100	1.7	a & b
14 ↓ 30	$C_{15}H_{24}O$ ↓ $C_{15}H_{24}O$	-	16.7	a

Legend: a = mass fragmentation; b = coinjection with authentic sample; i = correct isomer not characterised; t = tentatitive identification; *KI of compounds on PEG 20M column was also determined.

(Figure 1). From the analysis of mass fragmentation pattern, the unidentified compounds were assigned the formula $C_{15}H_{24}O$ which indicated that they were also sesquiterpenoids hydrocarbons.

The main components of the leaf oil were the tricylic sesquiterpenoid, δ-cadinene, and the monocylic sesquiterpene, β-bisabolene, which comprised 47.2% and 20.0% of the oil respectively (Table 1). Nerolidol (4.7%), ß-caryophyllene (2.6%) and elemene (1.3%) were the other components present in significant amounts. The other sesquiterpenoids were γ-elemene, α-bergamotene, α-farnesene, α-humulene and β-sinensal.

The wood oil of Clausena lansium

Water distillation of the ground fresh wood of *C. lansium* yielded 1.6% of a colourless oil with a characteristic spicy odour. The gas chromatogram of the wood oil revealed the presence of at least 70 compounds but only 47 of them could be identified (Figure 2). Monoterpenes constituted more than 70% of the oil, in which β-phellandrene at 55.0% concentration was the most abundant compound (Table 2). Other major monoterpenes which were present in more than 1% concentration were α-pinene, p-cymene, terpinen-4-ol, sabinene, borneol, α-phellandrene, myrcene and linalool, arranged in decreasing order of

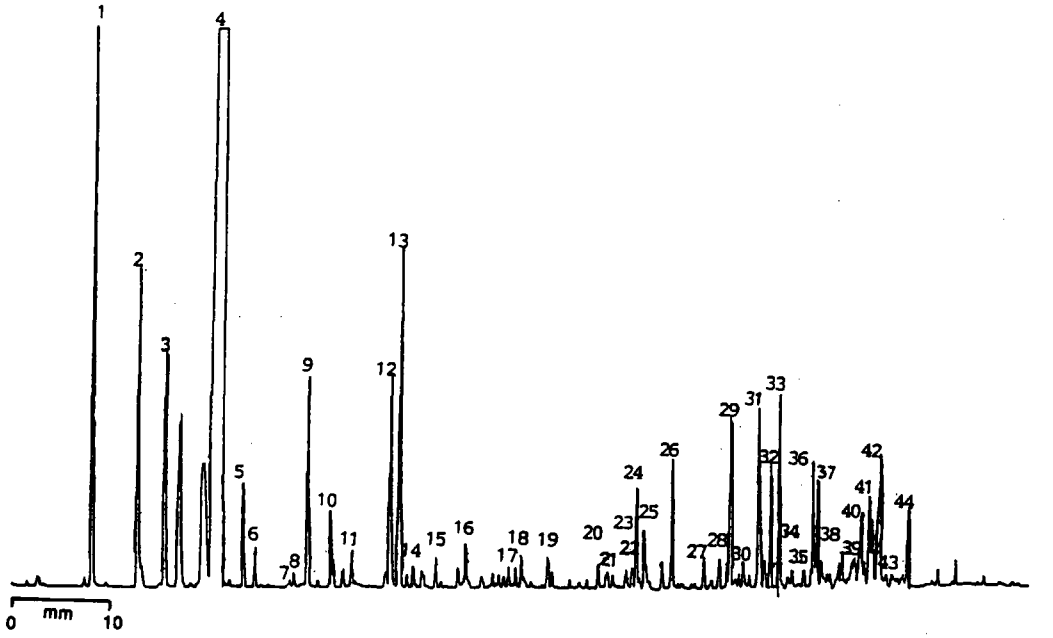

Figure 2. Gas chromatogram obtained with capillary SE 30 column for the wood oil of *Clausena lansium;* for identity of peaks, see Table 2

Table 2. Composition of the wood oil of *Clausena lansium*

(column: 25 m SE 30)

Peak number	Compound	Retention indices (*KI)	%	Identified by
1	α-pinene	936	4.0	a & b
2	sabinene	968	2.3	a & b
3	myrcene	983	1.8	a & b
4	α-phellandrene	998	1.9	a & b
5	p-cymene	1015	2.6	a & b
6	β-phellandrene	1026	55.0	a & b
7	(E) - β-ocimene	1039	0.6	a
8	γ-terpinene	1057	0.2	a
9	linalool oxide [i]	1075	tr	a
10	terpinolene	1081	0.2	a & b
11	linalool	1085	1.5	a & b
12	trans-p-menth-2-en-1-ol	1108	0.5	a
13	camphor	1126	0.3	a & b
14	borneol	1155	1.9	a & b
15	terpinen-4-ol	1166	2.6	a & b
16	α-terpineol	1175	0.2	a & b
17	trans-carveol	1200	0.2	a
18	fenchyl acetate	1209	0.2	a
19	2, 4-dimethyl acetophenone	1216	0.2	a
20	geraniol	1235	0.1	a & b
21	$C_{10}H_{16}O$	-	0.1	a
22	$C_{10}H_{16}O$	-	0.1	a
23	methyl nerate [i]	-	0.1	a
24	fenchene [i]	-	0.1	a
25	2,5,6-trimethyl-1,3, 6-heptatriene	1310	0.1	a
26	α-cubebene	1350	0.2	a & b
27	methyl methanthranilate [i]	1380	1.0	a
28	β-cubebene	1387	0.7	a & b
29	β-caryophyllene	1420	1.0	a & b
30	aromadendrene	1442	0.4	a & b
31	a-humulene	1454	0.2	a & b
32	γ-muurolene	1471	1.2	a
33	α-cadinene [i]	1480	0.2	a
34	α-farnesene	1496	2.0	a
35	γ-cadinene	1509	0.8	a
36	δ-cadinene	1515	1.3	a
37	elemol	1535	0.1	a
38	nerolidol [i]	1549	0.1	a & b
39	spathulenol	1566	0.9	a & b
40	levomenol [i]	1578	0.7	a
41	$C_{15}H_{24}O$	-	0.9	a
42	"	-	1.2	a
43	"	-	1.4	a
44	"	-	0.2	a
45	$C_{15}H_{24}O$	-	0.9	a
46	tetradecanal	1607	0.2	a & b
47	β-sinensal	1620	0.4	a

See Table 1 for legend.

concentration. γ-Terpinene, (E)-β-ocimene, linalool oxide, terpinolene, camphor, p-menth-2-en-1-ol, terpineol, geraniol, trans-carveol, α-fenchene, fenchyl acetate and methyl nerate were the other identified monoterpenes.

The 16 sesquiterpenoids identified accounted for 10.4% of the wood oil. Sesquiterpenoids that were present in more than 1% concentration were α-farnesene, δ-cadinene, β-caryophyllene and γ-muurolene. β-Cubebene, γ-cadinene, nerolidol, α-cubebene, aromadendrene, α-humulene, α-cadinene, elemol, levomenol, β-sinensal and spathulenol were the other sesquiterpenoids identified.

Conclusion

The unique profile of volatile compounds in different parts of the plant may contribute to the identification of this *Clausena* species. The high yield of oil containing aroma terpenoids obtained from the wood of *C. lansium* (1.60%) qualifies it to be a potential source of perfumery material.

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