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Identification of the Volatile Components in the Leaves and Wood of *Cunninghamia lanceolata.*

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Essential oil of the wood and leaves of ***Cunninghamia lanceolata*** was obtained from the chips by steam distillation. Following the further separation, 5 fractions of wood essential oil were obtained by column chromatography. Each fraction was then conduted in GC and GC-MS for identification of the components. Results indicate that cedrol was the major component accounting for 60.5% of the total essential oil. The other minor 39 compounds including α-cedrene, terpinyl acetate, etc were also presented. Among these, the 28 compounds including terpinyl acetate, and terpinolene etc were reported for the first time in the wood essential oil of *C. **lanceolata.***

In the essential oil of C. ***lanceolata*** leaves, α-limonene acconuting for 27.3% was the major component. There are other 19 components including a-pinene, and β-pinene etc were also identified.

INTRODUCTION

Cunninghamia Zanceolata (Lamb.) Hook was originated in southern porvinces of Mainland China. It is a very important tree species of silviculture in Taiwan. The wood volume was recorded 20,260,029 M^3 in 20,233 ha of C. *Zanceolata* forests in 1981 (unpublished data). Due to the existence of essential oil in the wood of C. *Zanceolata* (Shieh et al., 1977), it is resistant to decaying (Shieh et al., 1986, 1987, Shieh and Sumimoto 1991). It was mainly used in house and ship-building industry, and furniture. In recently, it was substituted by metals which hampered the utilization of C. *lanceolata*. Shieh et al., (1991 a, 1991 b, and 1991 c) reported recently for the first time that logs and sawdusts of C. *Zanceolata* can be used in cultivation of shiitake. The yields of shiitake were negatively related to the contents of essential oil in the log of C. *Zanceolata.*

Kafu (1917) reported that cedrol was the major components in the essential oil of C. *Zanceolata.* Beside that a-pinene, β-pinene, phellandrene, 1,8-cineole, camphene, terpineol, limonene, borneol and a-cedrene were also presented in it. However, research on the essential oils from the leaves was limited. This study was attempted to use GC-MS method, which may be more effective and precise than the traditional method, for the identification of the components in the essential oil from the leaves and

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woods of C. *lanceolata*.

MATERIALS AND METHODS

Materials

Logs and leaves of C. *lanceolata* were obtained from Lien-Hua-Chih Branch Station of the Taiwan Forestry Research Institute (TFRI) in central Taiwan.

Extraction for essential oils

The heartwood and sapwood of C. *lanceolata* were individually sawn into planks; they were then cut into shavings. Essential oils were obtained by steam distillation of the shavings for six hours.

Separation of the components in the wood essential oil

Separation method of essential oil component was the same as described in the previous paper (Shieh and Sumimoto 1991 c).

Wood essential oil was separated by column chromatography (95 ×5cm, silica gel). The separation procedure, Table 1, solvent and volume was n-hexane, 200ml; followed by n-hexane/ether (90/10, V/V), 1,200ml; n-hexane/ether (80/20, V/V), 800ml; n-hexane/ether (70/30, V/V), 800ml; n-hexane/ether (60/40, V/V), 800ml; n-hexane/ether (40/60, V/V), 800ml; n-hexane/ether (20/80, V/V), 800ml; and ether, 1200ml. The first two extracts were combined and named as fraction A., the 3rd extraction as fraction B., the 4th - the 6th extraction as fraction C., the 7th extraction as fraction D.. and the 8th extraction as fraction E.

Gas liquid chromatography (GLC) analyses

GLC analyses were conducted on a Chrompack model CP9000 gas chromatograph, equipped with a flame ionization detector (FID), and interfaced to a data processor.

Table 1. Separation of essential oil from the heartwood of C. *lanceolata* by column chromatography.

Exoraction solvent				
n-hexane: ether	Solvent volume	Fraction	Dry weight of extract (g)	Yield (%)
100: 0	200	A	2.8	9
90: 10	1200			
80: 20	800	B	0.8	2.5
70: 30	800			
60: 40	800	c	24.3	78.3
40: 60	800			
20: 80	800	D	1.5	4.8
0:100	1200	E	1.4	4.5

Note: Essential oil(31g) of C. *lanceolata* was separated by a silica gel colum chromatography (95 × 5cm. silica gel)

Separations were accomplished on a carbowax 20M packed in a 50m ×0.25mm fused silica capillary column. The injector and detector temperature was controlled at 250°C, nitrogen carrier gas at 2 ml/min; make up nitrogen flow at 30 ml/min, and the oven temperatures were programmed from 85°C to 220°C at a rising rate of 5°C/min for the leaves and wood essential oils, and from 110°C to 220°C at a rising rate of 4°C/min for each fraction of wood essential oil.

Gas chromatograph-Mass spectrometry (GC-MS)

Identification of the volatile compounds was conducted on a Shimadzu QP2000 GC -MS system. Gas chromatography equiped with a fused silica carbowax 20M capillary column (50 X 0.2mm i.d.; chrompack) was connected directly into the mass spectrometer. The injector temperature was at 250°C, the temperature program was controlled from 85 to 220°C at a rising rate of 5°C/min and it was controlled at 220°C for 50 min, carrier helium velocity was 1.8ml/min, electron energy was 70 eV.

RESULTS AND DISCUSSION

Variation of main component contents in the essential oil from the wood and leaves of C. lanceolata

All the components greater than 1% in the essential oil were listed in Table 2 and 3, respectively.

As shown in Table 2, cedrol, which accounted for 60.5%, was the major component in the essential oil of C. *Zanceolata* wood, following the components of a-terpineol, α -cedrene, and peak 22, that accounted for 15.4%, 6.5% and 4.5%, respectively. Other minor components were shown in Fig 1.

Because cedrol strongly inhibited the growth of bacteria (Shieh et al., 1986) and fungi (Shieh and Sumimoto, 1991 b), and it is the major component in the essential oil of C. *lanceolata*. That is the reason why C. *Zanceolata* wood is resistant to decaying while it is used as a coffin and buried in the soil for several decades. The reason why

Table 2. Variation of main component contents in the essential oil from the wood of C. ***Zanceolata.***

Peak No.	Compund	Contents of Compound (%)
6	a-cedrene	6.5[a)]
8	carotol	2.8
10	a-terpineol	15.4
20	cedrol	60.5
21	camphor(?)	3.0
22	veridiflorol(?)	4.5
23	$C_{15}H_{26}O$	1.7
28	1,4,7,10,13,16-hexaoxcyclooctadecane	2.1
29	tetradecane	2.0

Note: a) Counted by digital integrator.

C. lanceolata was considered to be imposible to grow shiitake on it was also due to the existence of cedrol or essential oil which inhibited the mycelial growth of shiitake.

As shown in Table 3, α-limonene, which accounted for 27.3%, was the major component in the essential oil of C. *lanceolata* leaves, following the components of α-pinene, β-myrcene, β-caryophyllene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl) naphthalene, and hedycaryol, they accounted 5 for 18.5, 9.6, 9.6, 7.4, and 6.5%, respectively. Other minor components were shown in Fig 2.

Volatile compound identified in the essential oils of C. lanceolata wood by GC-MS.

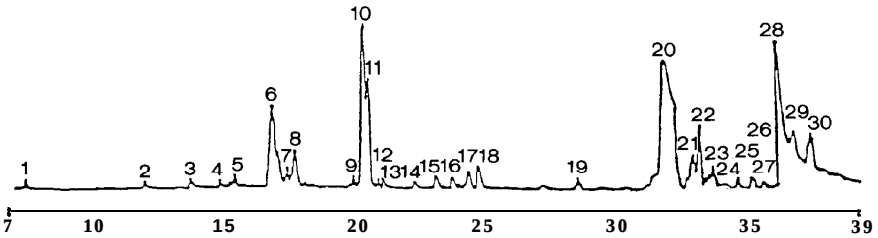


Fig.1 Chromatogram of essential oil from the wood of C. ***lanceolata.***
1. α-limonene 2. fenchone 3. 1-terpineol 4.β-himachalene 6. α-cedrene 10. α-terpineol ll.isoborneol acetate 12. 4-methyl-1-(1-methyl-ethl) bicyclo 3,10 hexan-3-ol(?) 13. isocaryophyllene 14. a-curcumene 15. 5,9-dimethyl-2-decanone(?) 17. p-cymen-8-ol 18. 6-methyl-5-hepten-2-one 20. cedrol

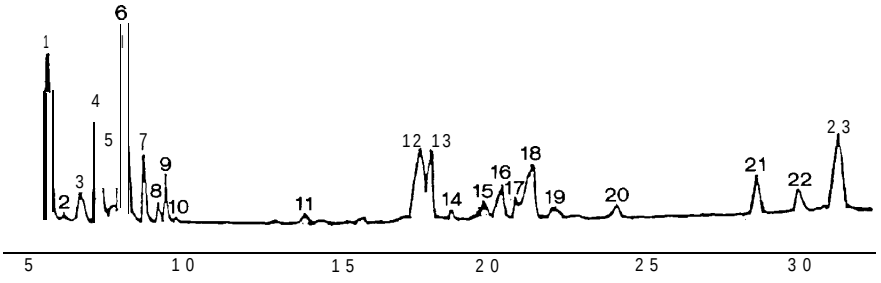
Table 3. Variation of main component contents in the essential oil from the leaves of C. ***lanceolata***

Peak No.	Identified Compund	Contents of Compound (%)
1	α-pinene	18.5"
3	β-pinene	2.5
4	β-myrcene	9.6
6	α-limonene	27.3
8	p-cymene	1.9
10	geraniol	2.0
12	isocaryophyllene(?)	5.6
13	β-caryophyllene	9.6
15	β-selinene	2.3
16	terpinyl acetate	1.7
18	decahydro-4a-methyl-1-methylene-7-(1-methylethenyl) naphthalene	7.4
21	germacrene B	2.4
22	nerolidol	1.5
23	hedycaryol	6.5

Note: a) Counted by digital integrator.

31 grams of the essential oil were passed through a silica gel column and 5 fractions were obtained as shown in Table 1. Each fraction was further separated and analyzed by GC-MS. As shown on Table 1, compound of the Fraction C was white crystal with a melting point at 85 –86° C. It is also possessed the special scent of China fir wood.

The mass spectrum (Fig. 3) of the crystal was found with a molecular peak at M+ =222, a parent peak at m/z=95 {[C_7H_{11}]+}, and a main peak at m/e=150 {[M-H_2O-C_4H_6]+}, 135 {[$C_{10}H_{15}$] + }, 107 {[C_8H_{11}]+}, and 161{[$C_{12}H_{17}$] + }.



Retention time

Fig.2 Chromatogram of essential oil from the leaves of C. ***lanceolata.***
1. α-pinene 2. camphene 3. β-pinene 4. β-myrcene 5. a-terpinene 6. a-limonene 7. 3-carene 8. p-cymene 9. terpinolene 10. geraniol 11. δ-elemene 12. 3,7-dimethyl-1, 6-octadien-3-ol 13. β-caryophyllene 14. y-elemene 15. β-selinene 16. terpinyl acetate 17. α-cubebene 18. decahydro-4a-methyl-1-methylene-7-(1-methyletheny) naphthalene(?) 19. δ-cadinene 20. germacrene B 21. 1 methyl-4-(2-methyloxiranyl) 7-oxabicyclo 4,1,0 heptane(?) 22. nerolidol 23. hedycaryol

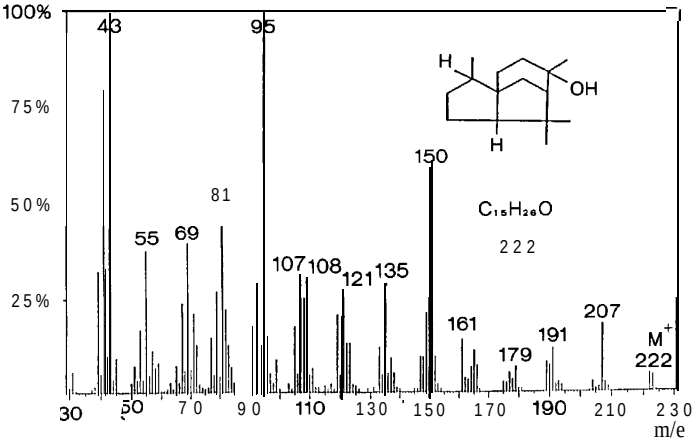


Fig.3 Mass spectrum of cedrol in the essential oil of C. ***lanceolata*** wood.

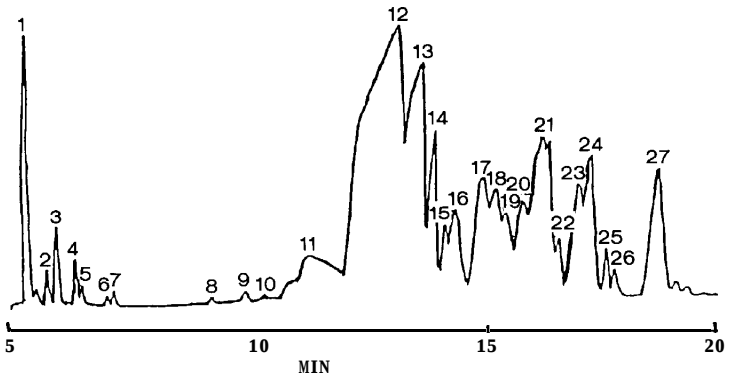


Fig.4 Chromatogram of fraction A separated from the essential oil of C. *lanceolata* wood.
1. α-pinene 2. β-pinene 3. tricyclene 4.α-limonene 5. β-phellandrene 6. p-cymene 7. terpinolene 8. 4-isopropenyl-1-methylbenzene 9. 1-terpineol 10. a-guaiene 11. β-himachalene 12. α-cedrene 13. carotol 14. thujopsene 16. β-sesquiphellandrene 17. acordiene 18. α-cubebene 19. δ-elemene 20. y-muurolene 21. y-elemene 22. germacrene B 23. δ-cadinene 24. a-curcumene 25. β-cedrene 26. α-muurolene 27. cuparene

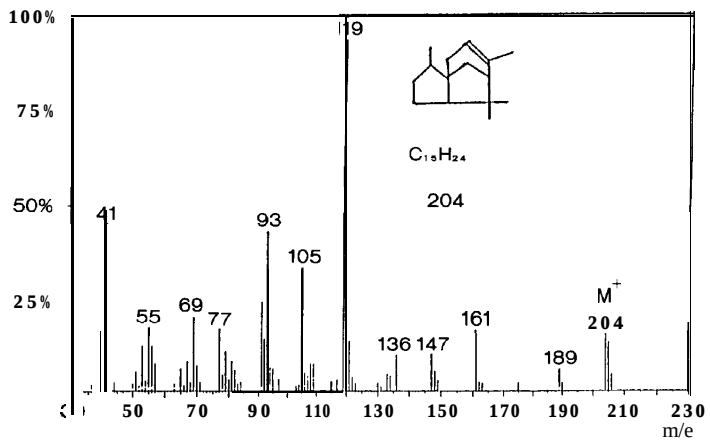


Fig.5 Mass spectrum of α-cedrene in the essential oil of C. *lanceolata* wood.

These were similar to the characteristics of a sesquiterpenic alcohol, $C_{15}H_{26}O$, and they were prety the same as that described in the reports of cedrol by Yukawa and Ito (1979), Shieh and Matsubara (1981) and (Shieh and Sumimoto (1991 c).

The chromatogram of the components of the fraction A, after GC-MS and GC, were shown in Fig 4. a-cedrene was major component in the fraction A and its mass spectrum was shown in Fig 5.

The chromatogram of the components of the fraction B was shown in Fig 6. Among the 7 identified compounds, terpinyl acetate, isopulegol, and isoborneol acetate

were reported for the first time in the essential oil of C. *Zanceolata.* Cedrol was the major component in the fraction B.

The chromatogram of the components of the fraction D was shown in Fig 7. Among the 10 identified compounds, thujopsene was also present in fraction A, isopulegol and cedrol were also present in fraction **B.**

The chromatogram of the components of the fraction E was shown in Fig 8. Among the 4 identified compounds, α-terpineol was also presented in fraction D.

The mass main fragments of all fractions were listed in Table 4. Identification was accomplished by comparing mass spectra with published data (Kafu, 1917; Yukawa and Ito, 1979; Shieh and Matsubara, 1981).

Cedrol was the major components in the essential oil of C. *Zanceolata.* Among the 40 identified components, 6-methyl-5-hepten-2-one, 4-isopropenyl-1-methylbenzene, p-cymene, tricyclene, terpinolene, p-cymen-8-ol, verbenone, fenchone, isopulegol, myrcenol, cis-linaloloxide, a-terpinyl acetate, tetradecane, α-curcumene, cuparene, acoradiene, isocaryophyllene, a-guaiene, β-himachalene, thujopsene, β-sesquiphellandrene, α-cubebene, δ-elemene, y-muurolene, germacrene B, δ-cadinene, α-muurolene, widdrol, were reported for the first time in the essential oil of C. *Zanceolata* wood.

Volatile components identified in the essential oil of C. lanceolata leaves by GC -MS.

As shown in Fig 2. a-limonene was the major component in the essential oil of C. *Zanceolata* leaves. The mass main fragments of all fractions were listed in Table 4. Among 20 identified components, p-cymene, α-limonene, a-pinene, β-pinene, terpinolene, a-terpinyl acetate, a-cubebene, germacrene B, and δ-cadinene were also presented in the essential oil of C. *Zanceolata* leaves. However, cedrol, which was the major component in the essential oil of C. *Zanceolata* wood, was not found in the essential oil of C. *Zanceolata* leaves.

CONCLUSION

Cedrol, which accounted for 60.50%, was the major components in the essential oil of C. *Zanceolata.* Forty minor components including a-cedrene were also identified. Among them, 28 components such as terpinolene etc. were reported for the first time in the essential oil of C. *Zanceolata* wood.

In the essential oil of C. *Zanceolata* leaves, a-limonene accounting for 27.3% was the major component. Other 19 components such as a-pinene, β-pinene were also identified.

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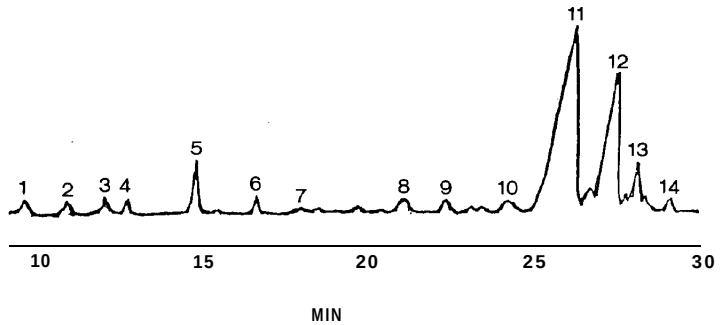

Fig.6 Chromatogram of fraction B separated from the essential oil of C. *lanceolata* wood.
1. 1-terpineol 2. isopulegol 3. isoborneol acetate 4. valencene 5. α-terpinyl acetate 6. a-curcumene 7. cuparene 11. cedrol 12. viridifloral(?)

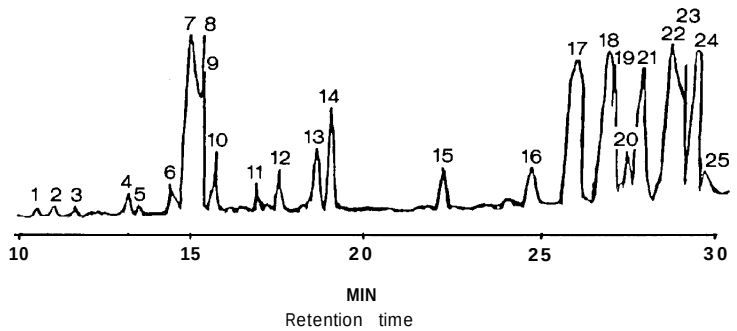

Fig.7 Chromatogram of fraction D separated from the essential oil of C. *Zanceolata* wood.
2. α-borneol 4. isopulegol 5. thujopsene 7. α-terpineol 8. borneol 9. isoborneol 10. verbenone 11.myrcenol 13.p-cymen-8-ol 17. cedrol 18. widdrol 20. cis-linaloloxide(?) 23. linalyl propanoate(?) 25. lavandulol(?)

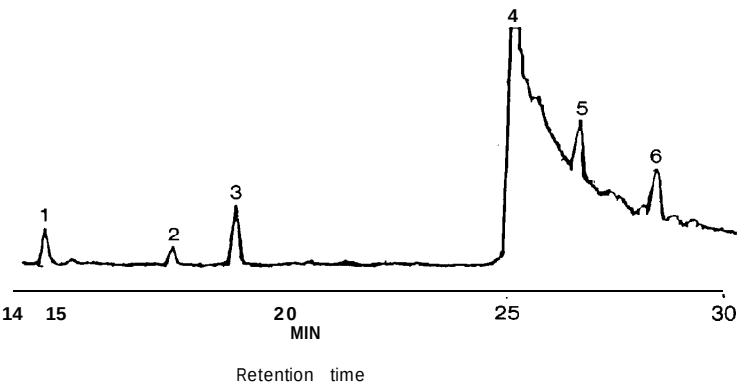

Fig.8 Chromatogram of fraction E separated from the essential oil of *C. lanceolata* wood.
1. a-terpineol 3. 6-methylhept-5-en-2-one 4. 1,4,7,10,13,16-hexaoxacyclooctadecane 6. tetradecane

Table 4. Volatile Compounds identified in the essential oils of C. ***lanceolata*** wood and leaves by GC-MS.

No.	Identified Compounds	m.wt.[1]	m.f.[2]	base main[3] peak	fragment m/e	Existence[4]
1	6-methyl-5-hepten-2-one	126	$C_8H_{14}O$	43	71,108,126,93	Wood[5] 18, Fe 3
2	4-isopropenyl-1-methylbenzene	132	$C_{10}H_{12}$	117	132,115,91,65	Fa[6] 8
3	p-cymene	134	$C_{10}H_{14}$	119	134,91,65,77	Fa 6, Leaf[7] 8
4	α-limonene	136	$C_{10}H_{16}$	68	67,93,53,79,107,121	Wood 1, Fa 4, Leaf 6
5	α-pinene	136	$C_{10}H_{16}$	93	91,92,77,41,79	Fa 1, Leaf 1
6	β-pinene	136	$C_{10}H_{16}$	93	41,69,77,79,91	Fa 2, Leaf 3
7	tricyclene	136	$C_{10}H_{16}$	93	41,79,77,91	Fa 3
8	β-phellandrene	136	$C_{10}H_{16}$	93	91,77,41,136,121	Fa 5
9	terpinolene	136	$C_{10}H_{16}$	93	121,136,41,79,92	Fa 7, Leaf 9
10	camphene	136	$C_{10}H_{16}$	93	41,121,79,67,136	Leaf 2
11	β-myrcene	136	$C_{10}H_{16}$	41	93,69	Leaf 4
12	a-terpinene	136	$C_{10}H_{16}$	121	93,92,41,136,77	Leaf 5
13	3-carene	136	$C_{10}H_{16}$	93	77.43.121.136	Leaf 7
14	p-cymen-8-ol	150	$C_{10}H_{140}$	43	135,91,117	Wood 17, Fd 13
15	verbenone	150	$C_{10}H_{140}$	107	80,135,91,150,55	Fd 10
16	fenchone	152	$C_{10}H_{160}$	81	69,41,152	Wood 2
17	geraniol	154	$C_{10}H_{180}$	69	41,93,111	Leaf 10
18	α-terpineol	154	$C_{10}H_{180}$	59	43,93,121,136	Wood 10. Fd 7
19	1-terpineol	154	$C_{10}H_{180}$	43	81,82,93,136	Fa 9. Fb 1.
20	isopulegol	154	$C_{10}H_{180}$	41	71,93,55,121	Fb 2: Fd 4'
21	borneol	154	$C_{10}H_{180}$	95	110,41,55	Fd 8
22	isoborneol	154	$C_{10}H_{180}$	95	110,41,121	Fd 9
23	myrcenol	154	$C_{10}H_{180}$	59	43,79,93,68,121	Fd 11
24	isoborneol acetate	196	$C_{12}H_{20}O_2$	43	95,93,121,136	Wood 11, Fb 3
25	α-terpinyl acetate	196	$C_{12}H_{20}O_2$	43	121.93.136	Fb 5, Leaf 16
26	tetradecane	198	$C_{14}H_{30}$	57	43,71,85,99,113	Fe 6
27	a-curcumene	202	$C_{15}H_{22}$	119	132,41,105,55,91	Wood 14, Fa 24, Fb 6
28	cuparene	202	$C_{15}H_{22}$	132	145,119,104,41,202	Fa 27, Fb 7
29	acoradiene	204	$C_{15}H_{24}$	119	41,93,105,121,161	Fa 17
30	isocaryophyllene	204	$C_{15}H_{24}$	41	93,105,69,121	Wood 13
31	α-guaiene	204	$C_{15}H_{24}$	105	106,147,93,204,41	Fa 10
32	β-himachalene	204	$C_{15}H_{24}$	119	41,93,105,161,204	Fa 11, Wood 4
33	α-cedrene	204	$C_{15}H_{24}$	119	41,93,69,161,105	Fa 12, Wood 6
34	thujopsene	204	$C_{15}H_{24}$	119	123,105,41,93,55	Fa 14, Fd 5
35	β-sesquiphellandrene	204	$C_{15}H_{24}$	69	41,93,55,161	Fa 16
36	a-cubebene	204	$C_{15}H_{24}$	161	105,119,41,91	Fa 18, Leaf 17
37	δ-elemene	204	$C_{15}H_{24}$	121	93,136,41,161	Fa 19
38	γ-muurolene	204	$C_{15}H_{24}$	161	105,41,91,81,119	Fa 20
39	germacrene B	204	$C_{15}H_{24}$	121	136,93,41,105	Fa 22, Leaf 20
40	δ-cadinene	204	$C_{15}H_{24}$	161	119,134,105,41,91	Fa 23, Leaf 19
41	β-cedrene	204	$C_{15}H_{24}$	119	105,93,41,55,69	Fa 25
42	a-muurolene	204	$C_{15}H_{24}$	105	161,81,41,93,94	Fa 26
43	β-caryophyllene	204	$C_{15}H_{24}$	41	69,93,133,92,79	Leaf 13
44	y-elemene	204	$C_{15}H_{24}$	121	93,41,107,81	Leaf 14
45	β-selinene	204	$C_{15}H_{24}$	93	41,80.105,121	Leaf 15
46	α-cedrol	222	$C_{15}H_{26}O$	95	43,151,152	Wood 20, Fb 11, Fd 17
47	widdrol	222	$C_{15}H_{26}O$	43	95,151,109,69,81	Fd 18
48	nerolidol	222	$C_{15}H_{26}O$	41	43,69,93,55	Leaf 22
49	hedycaryol	222	$C_{15}H_{26}O$	59	43,93,161,107	Leaf 23
50	1,4,7,10,13,16-hexaoxacyclooctadecane	264	$C_{12}H_{24}O_6$	45	89,87,133	Wood 28, Fe 4

Note: [1]. m. wt.: Molecular weight
[2]. m. f. : Molecular formula
[3]. Main fragments in decreasing intensity order.
[4]. As sequential peak count number
[5]. Wood : The essential oil of *C. lanceolata* wood
[6]. Fa : Fraction A of the essential oil from *C. Zanceolata* wood
Fb : Fraction B of the essential oil from *C. lanceolata* wood
Fd : Fraction D of the essential oil from C. *lanceolata* wood
Fe : Fraction E of the essential oil from C. *lanceolata* wood
[7]. Leaf : The essential oil of C. *lanceolata* leaves

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