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Biogenesis of the Essential Oils in Camphor Trees. XXX.[1] On the Components of the Essential Oil of *Cinnamomum reticulatum* Hay. in Taiwan[2]

Yasuji FUJITA and Shin-ichi FUJITA*
Government Industrial Research Institute, Osaka, Midorigaoka, Ikeda-shi, Osaka
**College of Education, Mukogawa Women's University, Ikebiraki-cho, Nishinomiya-shi, Hyogo*

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Cinnamomum reticulatum Hay. [*Mat. Fl. Formos.* 239 (1911); *Icon. Pl. Formos.*, **5**, 160, f. 53, e (1915)] (Japanese name, *Hamagusu*) of the Lauraceae is an endemic plant growing only on the Hengchun (Kōsyun) Peninsula in Taiwan. It is a small tree which grows at low altitudes.[3]

We have examined the essential oil of this rare and very interesting plant. The yield of the oil is 0.56% in the fresh shoots, the chemical composition of the oil is in Table 1.

The characteristics of this oil are an abundance of *l*-linalool (as much as 97% of the oil), and an absence of camphor and phenol ethers.

These phenomena show that this plant may be a relic of the nearest species to the mother plant of the genus *Cinnamomum*, at least as seen from the viewpoint of the chemical systematics.[4] The existence of a small

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[1] Part XXIX: Y. Fujita, S. Fujita, and Y. Akama, *Nippon Nogeikagaku Kaishi*, **46**, 17 (1972).

[2] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[3] R. Kanehira, "Formosan Trees," revised, Department of Forestry, Government Research Institute, Formosa, Yōkendo, Tokyo (1936), p. 211.

[4] Y. Fujita, *Bot. Mag. Tokyo*, **80**, 261 (1967).

Table 1. The composition of the essential oil of *Cinnamomum reticulatum* Hay.

Peak No.	Compound	%	Remark
Monoterpenoids and other low boiling compounds			
1	α-Pinene	0.1	Rt.
2	Camphene	0.3	Rt.
3	β-Pinene	0.5	Rt.
4	Limonene	0.2	Rt.
5	1,8-Cineole	0.4	Rt.
6	*p*-Cymene	0.2	Rt.
7	*cis*-β,γ-Hexenol (?)	0.1	
8	*trans*-Linalooloxide	trace	Rt.
9	*cis*-Linalooloxide	trace	Rt.
10	**l-Linalool**	**96.8**	Rt., IR[a]
11	unidentified alcohol	0.1	
12	Terpinen-4-ol	trace	Rt.
13	α-Terpineol	0.3	Rt.
14	Citronellol	trace	Rt.
15	Nerol	trace	Rt.
16	Geraniol	0.1	Rt.
17	unidentified alcohol	0.1	
Sesquiterpene hydrocarbons (0.4%to the oil)[b]			
18	α-Cubebene (?)	3	
19	Copaene	8	IR,[c]
20	β-Cubebene	4	IR
21	β-Elemene	2	IR
22	Caryophyllene	5	Rt., IR
23	unidentified	6	
24	α-Humulene	5	Rt., IR
25	β-Bisabolene (?)	7	IR
26	δ-Cadinene	54	Rt., IR
27	unidentified	4	
28	Calamenene	2	IR
Sesquiterpene alcohols (0.2% to the oil)[d]			
29	Nerolidol	15	Rt.
30	Elemol	7	Rt.
31	unidentified	4	
32	unidentified	7	
33	unidentified	7	
34	α-Cadinol	60	Rt., IR

a) This linalool (99.5% purity) isolated from the fractions II and III, had the following properties: d_4^{30} 0.8607, n_D^{30} 1.4582, $[\alpha]_D^{25}$ −20.03°. The specific optical rotation shows a perfect optical purity.

b) The sesquiterpene hydrocarbon part (about 50 mg) was separated from the fraction IV by chromatography on alumina, using *n*-hexane as the eluent.

c) Identification by IR spectra (J. A. Wenninger, R. L. Yates, and M. Dolinsky, *J. Ass. Offic. Anal. Chem.*, **50**, 1313 (1967)).

d) The compositions of sesquiterpene alcohols were calculated from the gas chromatogram of the oxygenated compounds, separated from the fraction IV by chromatography using ether as the eluent.

amount of nerolidol as a sesquiterpenoid compound is also accordant with this supposition.

Experimental

Material. On September 4, 1969, the material was gathered from a tree (diameter of trunk at a height of one meter: 15 cmϕ; height of the tree: *ca.* 7 m) which had been transplanted from the seashore to the garden of the Hengchun Branch of the Forestry Institute of Taiwan. The material (2.0 kg; the average length of a shoot: 23 cm; its weight: 11.0 g, consisting of 82% leaves, and 18% branchlets; size of leaf: 30×50 mm) was brought to Japan by air, and on September 10 the half-dried sample (1.2 kg) was subjected to steam distillation. The distilled oil was extracted with ether and then dried over anhydrous sodium sulfate. The oil (11.2 g), obtained in a yield 0.56% of the fresh material, had the following properties: d_4^{30} 0.8493, n_D^{30} 1.4584, α_D^{27} −14.40°, A.V. 0.25, E.V. 4.60.

Gas-liquid Chromatographic Analysis. The gas-liquid chromatography (glc) was carried out with a Shimadzu GC-1B Model apparatus equipped with a thermal conductivity detector. A 150×0.5 cm stainless steel column was packed with PEG 6000 (30%) on celite 545 (100 mesh). Hydrogen was used as the carrier gas. The percentages of the constituents of the oil were calculated from the areas of the peaks of the gas chromatogram.

Separation and Identification of the Individual Components. The oil (10.0 g) was fractionated, by distillation under reduced pressure in a current of nitrogen with a Widmer column, into the following four fractions: I, −87°C/20 mmHg, 1.0 m*l*; II, 87—89°C/20 mmHg, 3.0 m*l*; III, 89°C/20 mmHg, 2.0 m*l*; IV, residual, 4.5 g.

Each fraction was then further separated into hydrocarbons and oxygenated compounds by alumina-column chromatography. The main components were isolated by preparative glc using a PEG 6000 column and were identified by a comparison of the IR spectra and retention times (*Rt.*) of glc with those of authentic samples. Some minor compounds were identified by a comparison of the *Rts.* with those of authentic samples by the use of PEG 6000 and Silicone DC-550 columns.

The results are shown in Table 1.

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