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Biogenesis of the Essential Oils in Camphor Trees. XXVI. On the Components of the Essential Oil of *Cinnamomum daphnoides* Sieb. et Zucc.*[1]

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Cinnamomum daphnoides Sieb. et Zucc. (Japanese name, Marubanikkei) of Lauraceae is an endemic plant growing chiefly on the shores of the Osumi Peninsula and the Islands of Tane and Yaku in Kagoshima Prefecture, Japan.[1)]

This plant had been utilized as a linalool resource since a field survey of the senior author on Tane and Yaku Islands in 1947.[2)] Nakahara has reported that the plant obtained from Tane Island affords the essential oil in a 0.25% yield by the steam distillation of the twigs, and that the oil contains *l*-linalool (65—70%) and an unidentified high-boiling compound (15%) as the main components, besides α-pinene, *p*-cymene, cineole, and an ester.[3)]

The present investigation consists of the further study of this essential oil from the viewpoint of chemical systematics; in this paper, the authors will report on the results of their examination of the essential oil of the plant, bred from seeds collected on Tane Island in 1947.

The essential oil was obtained in a 0.15% yield by the steam distillation of fresh leaves and branchlets. The chemical composition of this oil is shown in Table 1. The characteristic of the oil is the abundant existence of *l*-linalool (69—75%) and elemicine (16—19%), the total amounting to 88.2—90.6%; the content of camphor is so small that it is not detected by the ordinary procedure.

A comparison with the essential oils of the relative species will be published later.

Experimental

Materials. Two plants in an experimental garden (Ikeda, Osaka), bred from seeds collected from a tree at Nishino-omote, Tane Island, Kagoshima Prefecture, on November 8, 1947.

Isolation of the Essential Oils. Sample I. On July 25, 1962, material gathered at the beginning of the flowering stage (21.7 kg) (the average length of a twig: 44 cm; its weight: 48 g, consisting of 69% leaves, plus a small amount of flowers, and 31% branchlets) was subjected to steam distillation. The distilled oil was extracted with ether, and then dried over anhydrous sodium sulfate. The oil (33.4 g) obtained in a 0.15% yield had the following properties: d_4^{30} 0.9208, n_D^{30} 1.4784, α_D^{10} −12.45°, A.V. 7.0, E.V. 3.1.

Sample II. On October 15, 1964, material gathered at fruiting stage (18.2 kg) (the average length of a twig: 44 cm; its weight: 42 g, consisting of 57% leaves, 42.6 % branchlets, and 0.4% fruits) was subjected to steam distillation; the oil (27.5 g) thus obtained in a 0.15% yield had the following properties: d_4^{30} 0.9077, n_D^{30} 1.4765, α_D^{10} −12.80°, A.V. 7.0, E.V. 2.4.

Gas-chromatographic Analysis. The gas chromatography was carried out by means of Shimadzu GC-1B Model equipment with a thermal conductivity detector. A 150×0.5-cm stainless steel column was packed with PEG 6000 (30%) on Celite 545 (100 mesh), and hydrogen was used as the carrier gas.

Separation and Identification of the Individual Components. The essential oil was fractionated by

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1) Y. Fujita, *J. Jap. Bot.*, **28**, 255 (1953); *Bot. Mag. Tokyo*, **80**, 216 (1967).

2) Y. Fujita, *Koryo*, **3**, 33 (1948).

3) K. Nakahara, Abstract of the Reports of the Annual Meeting of the Chem. Soc. of Japan, **5**, 105 (1952).

Table 1. Compositions of the essential oils of *C. daphnoides*

Peak No.	Rt.* (min)		Component	Sample I (%)	Sample II (%)	Remark
	A	B				
1	1.7		α-Pinene	0.5	0.5	
2	2.2		Camphene	0.3	0.3	
3	2.6		β-Pinene	0.3	0.3	
4	3.3		Limonene	0.4	0.3	IR
5	3.6		1,8-Cineole	1.0	1.0	IR
6	4.3		*p*-Cymene	0.2	0.2	IR
7	4.8		*n*-Hexanol	0.2	0.1	IR
8	5.6		*cis*-3-Hexen-1-ol	0.2	0.2	IR
9	6.5		unidentified alcohol	trace	0.1	
10	8.0	3.8	*trans*-Linalooloxide	0.5	0.4	IR
11	8.8	4.2	*cis*-Linalooloxide	0.5	0.3	IR
12	11.0	4.8	*l*-Linalool	**69.4**	**74.5**	IR, a
13		4.8	α-Ylangene	0.1	0.1	
14	14.0		Linalyl acetate	0.2	0.2	
15	16.5	5.9	unidentified alcohol	0.5	0.3	b
16	16.5	5.9	Camphor	trace	trace	
17		6.5	Terpinen-4-ol	0.2	0.2	
18		6.5	β-Elemene	trace	trace	
19		7.4	Caryophyllene	1.0	1.0	IR
20		8.8	α-Terpineol	0.6	0.5	IR
21		8.8	unidentified sesquiterpene hydrocarbon (S. H. C.)	trace	trace	
22		9.6	*trans*-2,6,6-Trimethyl-2-vinyl-5-hydroxy-tetrahydropyran	0.1	0.1	IR
23		9.6	Humulene	0.3	0.2	
24		10.0	*cis*-2,6,6-Trimethyl-2-vinyl-5-hydroxy-tetrahydropyran	0.1	0.1	IR
25		10.2	unidentified S. H. C.	0.3	0.2	
26		12.0	Nerol	0.3	0.1	
27		12.0	δ-Cadinene	0.4	0.2	
28		14.0	Geraniol	0.5	0.3	IR
29		14.0	unidentified S. H. C.	0.1	trace	
30		17.5	Safrole	0.3	0.2	
31		17.5	unidentified S. H. C.	trace	trace	
32		19.5	unidentified S. H. C.	trace	trace	
33		27.0	Methyleugenol	0.6	0.3	
34		45.0	Eugenol	1.7	1.5	IR
35		58.5	Elemicine	**18.8**	**15.8**	IR, c
36		63.0	Chavicol	0.2	0.2	

* A: 145°C, 60 m*l*/min H_2, B: 165°C, 80 m*l*/min H_2 on PEG 6000 column (5 mmφ × 1.5 m).

a) d_4^{30} 0.8690, n_D^{30} 1.4571, α_D^{19} −17.50°.

b) This compound shows the bands at 3400, 1100, 885 cm^{-1}.

c) Bp 272°C/756 mmHg, d_4^{30} 1.0519, n_D^{30} 1.5228. Trimethylgallic acid (mp 169°C) was obtained by oxidation with potassium permanganate.

distillation under reduced pressure into nine fractions. Each fraction was further divided into hydrocarbons and oxygenated compounds by alumina-column chromatography.

The components were isolated by preparative gas chromatography using a PEG 6000 column (2 m × 10 mmφ) and were identified by a comparison of the IR spectra and retention times (Rt.) with those of authentic samples. Some minor components were identified by Rt's. only using two kinds of columns (PEG 6000 and Silicone DC-550).

The results are shown in Table 1.