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Biogenesis of the Essential Oils in Camphor Trees. XXVIII.[1] On the Components of the Essential Oil of *Cinnamomum japonicum* Sieb.[2]

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Cinnamomum japonicum Sieb. is sometimes divided into several varieties on the basis of morphological differences in the leaves. The essential oils of samples of this plant from various parts in Japan were examined from the viewpoint of chemotaxonomy. The results obtained from the materials gathered at Mt. Satsuki, Ikeda-shi, Osaka Prefecture, will be reported here first. The characteristics of the oil of the leaves and branchlets are the abundant presence of 1,8-cineole and *p*-cymene. The rich existence of linalool in the branchlet oil may also be a characteristic of this plant.

Cinnamomum japonicum Sieb. (=*C. pedunculatum* Nees) (Japanese name, "Yabunikkei") of the Lauraceae grows widely in Japan–on Honshu, Shikoku, Kyushu, and the Ogasawara Islands; Fukushima Prefecture is the northern-most limit of its distribution. The Ryukyu Islands, Formulsa, the southern part of Korea, and Southern China are also in the area of geographical distribution of this plant. Sometimes this plant is divided into several varieties on the basis of morphological differences in the leaves.[3]

Many years ago, the essential oil of this plant was examined by Keimatsu *et al.*[4] They obtained the oil in a yield of about 1% by the steam distillation of bark from Hachijyo Island, Japan. The oil contained α-phellandrene (33%) as the main component, plus eugenol and methyleugenol. Shinozaki[5] examined the essential oil obtained in a yield of about 1% from the fresh leaves of plants of the Ogasawara Islands, and showed the presence of safrole (60%), eugenol (9%), and other compounds in the oil. Nakahara[6] also reported that plants obtained from Tane Island in Kagoshima Prefecture afforded the essential oil in a 0.3% yield, and that the oil contained camphor (25%) and cineole (16%), together with *p*-cymene and methyleugenol.

Since 1954, a careful comparison of the essential oils obtained from materials gathered from various localities in Japan has been performed in our laboratory

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[1] Part XXVII: Y. Fujita, S. Fujita, and S. Nishida, *Nippon Kagaku Zasshi*, **91**, 737 (1970).

[2] Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[3] T. Makino and K. Nemoto, "Flora of Japan," Nippon Shokubutsu Soran Pub. Assoc., Tokyo (1925), p. 924; S. Hatusima and T. Amano, "Flora of Okinawa," The Ryukyu Univ. Press, (1958), p. 34; G. Masamune, "A List of Vascular Plants of Taiwan." Hokuriku no Shokubutsu no Kai Press, (1954), p. 49; H. Liou, "Laur. Chin. Indochin.," Hermann Co., Paris (1934), p. 22; Y. Fujita, *Report of Govern. Ind. Res. Insti., Osaka*, **306**, 22 (1955); *Bot. Mag. Tokyo*, **80**, 262 (1967).

[4] S. Keimatsu and Y. Asahina, *Yakugaku Zasshi*, **26**, 1095 (1906).

[5] E. Shinozaki, *Kogyo Kagaku Zasshi*, **18**, 913 (1915).

[6] K. Nakahara, Report of 18th Congress of Camphor Industry Engineers, (1953), p. 41.

from the view-points of chemical systematics and chemical taxonomy.

In this paper, the results of our examination of the components of the essential oils obtained from materials gathered at Mt. Satsuki in Ikeda-shi, Osaka Prefecture, will be reported.

Experimental

Isolation of the Essential Oils. *Sample I*: On May 24, 1954, the material (average weight of a twig: 65 g, consisting of 68% leaves and 32% branchlets) was gathered from a tree (diameter of the trunk at a height of one meter; 9 cmϕ) at Mt. Satsuki, in Ikeda-shi, Osaka Prefecture (320 m above sea level). On May, 25, this material (19.9 kg) was subjected to steam distillation. The distilled oil was extracted with ether, and then dried over anhydrous sodium sulfate. The oil (67.1 g), obtained in a 0.34% yield, had the following properties: d_4^{30} 0.8939, n_D^{30} 1.4800, α_D^{28} $-11.00°$, A.V. 0.5, E.V. 1.0.

Samples of II: On April 22, 1954, the material (average weight of a twig: 120 g, consisting of 59% leaves and 41% branchlets) was gathered from another tree (diameter: 15 cmϕ) in the same locality. The material was divided into leaves and branchlets.

II-A: On April 23, the leaves (20.0 kg) were subjected to steam distillation; the oil (168.0 g), obtained in a 0.84% yield, had the following properties: d_4^{30} 0.8792, n_D^{30} 1.4781, α_D^{28} $-19.75°$, A.V. 0.2, E.V. 5.0.

II-B: On April 26, the branchlets (5.5 kg) were distilled with steam; the oil (8.3 g), obtained in a 0.15% yield, had the following properties: d_4^{30} 0.9522, n_D^{30} 1.4869, α_D^{28} $-9.00°$, A.V. 1.0, E.V. 12.8.

Gas-liquid Chromatographic Analysis. The gas-liquid chromatography (glc) was carried out with a Shimadzu GC-1B Model apparatus, equipped with a 150 × 0.5 cm stainless steel column containing 30% PEG 6000 or 30% Silicone DC-550 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 neutral part of the sample II-A (143 g) was fractionated, by distillation under reduced pressure in a current of nitrogen with a Widmer column, into eleven fractions, as is shown in Table 1. 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 components were identified by a comparison of the *Rt's* with those of authentic samples obtained by the above two kinds of columns.

TABLE 1. RESULTS OF FRACTIONAL DISTILLATION OF THE NEUTRAL OIL (SAMPLE II–A)

Fract.	Bp (°C/mmHg)	Dist. (m*l*)	Bp (°C/764 mmHg)	d_4^{30}	n_D^{30}	α_D^{22}(°)
I	—83/50	25	178	0.8548	1.4719	−24.45
II	83—87/50	30	179	0.8593	1.4750	−21.80
III	87—90/50	25	179	0.8642	1.4769	−12.55
IV	90—96/50	5	180	0.8662	1.4779	−4.60
V	96—118/50	5	189	0.8747	1.4811	−7.35
VI	118—120/50	5	207	0.8929	1.4810	−12.00
VII	—104/30	5	223	0.9271	1.4819	−22.45
VIII	—115/20	5	225	0.9313	1.4819	−23.25
IX	115—122/20	5	231	0.9385	1.4902	−15.30
X	122—125/20	7	269	0.9522	1.4975	−11.45
XI	Residual	—	—	—	—	—

TABLE 2. THE COMPOSITIONS OF THE ESSENTIAL OILS OF *C. japonicum* COLLECTED AT MT. SATSUKI, IKEDA-SHI, OSAKA PREF.

Peak No.	Compound	Sample I (Twigs) (%)	Sample II-A (Leaves) (%)	Sample II-B (Branchlets) (%)
1	α-Pinene	2.7	3.7	0.3
2	Camphene	0.1	0.5	0.1
3	β-Pinene	2.4	3.0	0.2
4	β-Myrcene	4.7	4.7	0.9
5	*l*-α-Phellandrene	2.8	7.7	0.2
6	Limonene	2.0	3.0	0.2
7	1,8-Cineole	**23.7**	**16.5**	**12.0**
8	*p*-Cymene	**45.2**	**40.0**	**24.1**
9	3-Hexen-l-ol	0.4	0.3	0.2
10	unidentified ketone	trace	trace	trace
11	*trans*-Linalool oxide	0.1	0.1	1.3
12	*cis*-Linalool oxide	0.1	0.2	1.2
13	*l*-Linalool	3.3	2.8	**23.5**
14	*l*-Copaene	0.3	0.9	1.4
15	Camphor	0.2	0.4	0.6
16	unidentified alcohol	0.2	0.3	0.5
17	SHC	trace	0.2	0.2
18	Terpinen-4-ol	1.6	2.4	4.1
19	β-Elemene	0.1	0.2	0.4
20	*l*-Caryophyllene	1.2	0.6	0.1
21	unidentified alcohol	—	—	0.6
22	SHC	0.3	0.1	—
23	*l*-α-Terpineol	3.7	1.6	3.2
24	α-Terpinyl acetate	0.4	2.0	7.0
25	*l*-Carvotanacetone	0.1	0.5	0.2
26	α-Humulene	0.2	0.5	0.3
27	SHC (ε-Cadinene ?)	trace	trace	0.1
28	Citronellol	trace	trace	1.5
29	SHC	0.1	0.5	0.5
30	*d*-δ-Cadinene	0.4	1.0	1.1
31	Nerol	0.2	trace	trace
32	SHC	trace	0.2	trace
33	*l*-*trans*-Yabunikkeol[9]	0.5	0.5	2.5
34	Geraniol	trace	trace	1.3
35	unidentified alcohol	trace	trace	trace
36	Calamenene	0.3	0.1	0.4
37	Safrole	trace	trace	trace
38	*d*-*cis*-Yabunikkeol[9]	0.4	0.6	1.3
39	α-Calacorene	trace	0.1	0.1
40	β-Calacorene	trace	trace	0.1
41	unidentified alcohol	trace	trace	trace
42	Methyleugenol	0.2	0.1	0.5
43	Elemol	0.7	1.3	2.6
44	unidentified ketone	trace	trace	0.1
45	unidentified alcohol	trace	trace	trace
46	Eugenol	0.7	1.5	1.4
47	α-Cadinol	0.5	1.2	2.2
48	unidentified	trace	trace	1.0
49	*l*-Kaurene	trace	trace	0.5

SHC: unidentified sesquiterpene hydrocarbon

The main components may be identified as follows:

l-α-Phellandrene: Peak 5 ($[\alpha]_D^{20}$ −158.0°, $c=2.2$, in $CHCl_3$) was isolated from fractions I—III; it was identified as α-phellandrene by a comparison of the IR spectra.7)

l-Linalool, Terpinen-4-ol, and l-α-Terpineol: Peak 13 ($[\alpha]_D^{20}$ −15.4°, $c=4.2$, in EtOH), peak 18, and peak 23 ($[\alpha]_D^{20}$ −49.6° $c=4.4$, in EtOH) were isolated from fraction VI and were identified as linalool, terpinen-4-ol, and α-terpineol respectively by a study of the IR spectra and *Rt's* in glc.

l-Carvotanacetone: Peak 25 ($[\alpha]_D^{20}$ −38.6°, $c=4.8$, in EtOH) was identified as carvotanacetone by a comparison of the IR spectrum8) and *Rt* with those of a synthetic sample prepared from carvone.

Citronellol, Nerol, and Geraniol: A mixed sample of fractions V and VI was heated with phthalic anhydride at 80°C in a pyridine solution for one hour; the esterified part was then extracted with a sodium hydrogencarbonate solution, the sodium salt of the phthalic acid esters was saponified by potassium hydroxide, and the regenerated alcohols were distilled with steam.

These primary and secondary alcohols (peak 28, 31, and 34) were separated by preparative glc and were identified as citronellol, nerol, and geraniol respectively by a study of the IR spectra and *Rt's*.

l-trans-*Yabunikkeol and* d-cis-*Yabunikkeol*: These new monoterpene alcohols9) (peaks 33 and 39) were also obtained from the above regenerated oil.

l-Copaene, β-Elemene, l-Caryophyllene, and β-Humulene: These sesquiterpene hydrocarbons (peaks 14, 19, 20, and 26) were isolated from fractions V—VIII and were identified as copaene ($[\alpha]_D^{20}$ −16.0°, $c=4.1$, in $CHCl_3$), β-elemene, caryophyllene ($[\alpha]_D^{20}$ −8.8°, $c=1.7$, in $CHCl_3$), and β-humulene respectively by a comparison of the IR spectra.10)

d-*δ-Cadinene, Calamenene, α-Calacorene, and β-Calacorene*: These sesquiterpene hydrocarbons (peak 30, 36, 39, and 40) were also identified as δ-cadinene ($[\alpha]_D^{20}$ +45.6°, $c=4.1$, in $CHCl_3$), calamenene, α-, and β-calacorene by a comparison of the IR spectra with those of authentic samples.10)

l-Kaurene: Peak 49 (mp 47°C, $[\alpha]_D^{20}$ −56.6°, $c=4.6$, in $CHCl_3$) was isolated from the residual oil of fractional distillation by column chromatography and was identified as kaurene by a study of the IR spectrum.11)

Results and Discussion

The yields of the essential oils of this *C. japonicum* are 0.34% from the fresh twigs (sample I), 0.84% from the leaves (sample II-A), and 0.15% from the branchlets (sample II-B). Table 2 shows the compositions of these oils.

From these results, we can see it is characteristic of the oil that 1,8-cineole and *p*-cymene exist abundantly, while there are only small amounts of camphor and phenol ethers. The abundance of *l*-linalool in the branchlet oil may also be a characteristic of this plant, though the components of these oils are almost the same.

Among the other substances, we could isolate two new monoterpene alcohols, named *trans*-yabunikkeol and *cis*-yabunikkeol (*trans*- and *cis-p*-mentha-1(7),5-dien-2-ol), for the first time;9) we also isolated *l*-kaurene, probably for the first time, in the Angiospermae.

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7) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965).

8) V. E. Veijola and A. D. Ilvespää, *Acta Chem. Scand.*, **13**, 301 (1959).

9) Y. Fujita, S. Fujita, and H. Yoshikawa, This Bulletin, **43**, 1599 (1970).

10) J. A. Wenninger, R. L. Yates, and M. Dolinsky, *J. Ass. Offic. Anal. Chem.*, **50**, 1313 (1967); J. Plíva, M. Horák, V. Herout, and F. Šorm, "Die Terpene," I, Akademie-Verlag, Berlin (1960).

11) The Infrared Data Committee of Japan, "IRDC card," No. 3306.