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Comparative Biochemical and Chemo-taxonomical Studies of the Essential Oils of *Magnolia salicifolia* Maxim. III[1,2]

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Essential oils of the methylchavicol type *Magnolia salicifolia* Maxim. were examined. The yields of oils were 0.78—1.06% of fresh shoots, 1.42% of fresh leaves, 0.51% of branchlets, 3.80% of fresh flower buds, and 0.92% of fresh flowers. The shoot oil contained 69.1—84.1% of methylchavicol and the leaf oil contained as high as 91.4% of methylchavicol, but the oil from branchlets contained 23.8% of 1,8-cineole, 19.7% of citral-b, and 30.2% of citral-a, and the oils from buds and flowers also contained 22.6—24.2% of citral-b and 38.1—43.3% of citral-a, as in the case of the anethole type, and the methylchavicol, safrole, and methyleugenol type *M. salicifolia*.

The oil of *Magnolia kobus* DC. examined by Asahina, *et al.* was not the oil of a true *Magnolia kobus* but was an oil of this methylchavicol type *Magnolia salicifolia*.

Essential oils of *Magnolia salicifolia* Maxim. (Japanese name, "Tamushiba") gathered from various localities in Japan are being compared for chemical taxonomy and chemical systematics.

In the preceding papers of this series, we have reported the composition of essential oils of the methylchavicol, safrole, and methyleugenol type[4] and that of the anethole type[2] of this plant. In this paper, the result of examination of the essential oils of the methylchavicol type trees will be reported.

Yield of essential oils was 0.78—1.06% of the fresh leaves and branchlets (sample I, II, III, and IV), and yields were also 1.42% of the fresh leaves (sample V_A), 0.51% of the branchlets (sample V_B), 3.80% of the fresh flower buds (sample V_C), and 0.92% of the fresh flowers (sample V_D). Chemical composition of these oils is shown in Tables I and II.

The characteristic of the oil from shoots is the abundant presence of methylchavicol (1-allyl-4-methoxybenzene) (69.2—84.1% in the oil of shoots and 91.4% in the oil of leaves). In contrast, the oil of branchlets is rich in 1,8-cineole (23.8%), citral-b (19.7%), and citral-a (30.2%), and the oils of buds and flowers contain a large amount of citral-b (22.6—24.2%) and citral-a (38.1—43.3%), similar to the methylchavicol, safrole, and methyleugenol type or the anethole type.

In 1908, Asahina, *et al.*[5] reported an analysis of a commercial oil of "Kobushi" obtained probably from the shoots collected in Shizuoka Prefecture, giving the following data: d^{20} 0.892, $[\alpha]_D$ +6°8′, A.V. 4.3, E.V. 19.1; and methylchavicol (the main component), together with citral (7%), pinene (?), cineole, and eugenol. These data agree with those of the oil

1) This forms Part XL of a series entitled "Miscellaneous Contributions to the Essential Oils of the Plants from Various Territories." Part XXXIX: S. Fujita and Y. Fujita, *Yakugaku Zasshi*, **95**, 475 (1975).
2) Part II: S. Fujita and Y. Fujita, *Chem. Pharm. Bull.* (Tokyo), **22**, 707 (1974). A part of this work was presented at the 249th Kansai Meeting of the Society of Agricultural Chemistry of Japan, Kyoto, June 1968.
3) Location: *a) Ikebiraki-cho, Nishinomiya-shi, Hyogo, 663, Japan; b) Midorigaoka, Ikeda-shi, Osaka, 563, Japan.*
4) S. Fujita and Y. Fujita, *Chem. Pharm. Bull.* (Tokyo), **20**, 2251 (1972).
5) Y. Asahina and H. Nakamura, *Yakugaku Zasshi*, **28**, 1267 (1908).

TABLE I. Compositions of the Essential Oils of the Shoots (Leaves and Branchlets) of the Methylchavicol type *M. salicifolia* (%)

Peak No.[a)]	Component	Sample I Hyogo Pref.	Sample II Osaka Pref.	Sample III Osaka Pref.	Sample IV Hyogo Pref.
1	α-Pinene	0.6	0.3	0.2	0.1
2	Camphene	0.5	0.1	0.1	0.1
3	β-Pinene	1.3	0.8	0.2	0.2
4	Limonene	2.4	5.0	2.0	1.0
5	1,8-Cineole	3.3	2.4	4.1	3.2
6	*p*-Cymene	0.3	0.4	0.8	0.4
7	*cis*-Alloocimene	0.4	0.6	0.2	0.3
8	Unidentified	0.2	0.1	0.1	0.1
9	*trans*-Linalool oxide	0.1	0.1	0.1	0.1
10	Fenchone	0.2	0.2	0.1	0.2
11	*cis*-Linalool oxide	0.1	0.1	0.1	0.1
12	Linalool	0.6	0.2	0.2	0.3
13	Camphor	0.1	0.1	0.1	0.3
14	Terpinen-4-ol	0.5	0.8	0.1	0.3
15	Caryophyllene	0.2	0.2	0.1	0.2
16	Methylchavicol	**71.5**	**69.2**	**83.3**	**84.1**
17	α-Terpineol	0.2	0.2	0.2	0.3
18	Citral-b	4.0	3.2	1.2	2.0
19	Citral-a	6.7	3.9	2.0	2.9
20	Nerol	0.5	0.4	0.1	0.1
21	Geraniol	0.3	0.2	0.1	0.1
22	*trans*-Anethole	2.2	3.3	0.9	0.4
23	Safrole	1.6	3.3	0.2	0.7
24	Methyleugenol	1.5	3.5	1.5	1.0
25	*p*-Anisaldehyde	0.2	0.1	0.3	0.4
26	Eugenol	0.3	0.5	0.9	0.3
27	Unidentified	0.1	0.4	—	—

a) GLC: PEG 6000 (30%), 160°, 80 ml/min H_2

from this methylchavicol type *M. salicifolia* and not to those of the oil from true *M. kobus*.[6] The oil of the so-called *Magnolia kobus* DC. examined by Asahina, *et al.* was just the shoot oil of the methylchavicol type *M. salicifolia*.

Experimental

Material——Sample I : The material was collected at the top of Mt. Koganédakè (*ca.* 700 m alt.) in Taki District, Hyogo Prefecture, on July 30, 1967. The shoots (average length of a twig, 35 cm; its weight, 10.5 g; consisting of 78% leaves and 22% branchlets) were gathered from several trees.

Sample II : The material was collected at the top of Mt. Tendai (600 m alt.) in Minoo-shi, Osaka Prefecture, on October 29, 1967. The shoots (average length of a twig, 35 cm; its weight, 6 g; consisting of 66% leaves and 34% branchlets) were gathered from a germinated small tree.

Sample III : The material was collected at Noma-tōgé (560 m alt.) in Toyonō District, Osaka Prefecture, on June 18, 1968. The shoots (average length of a twig, 42 cm; its weight, 8 g; consisting of 75% leaves and 25% branchlets) were gathered from a tree 3 cm in diameter.

Sample IV : The material was collected at Mt. Dainichi (260 m alt.) in Kawabé District, Hyogo Prefecture, on November 6, 1968. The shoots (average length of a twig, 33 cm; its weight, 6 g; consisting of 67% leaves and 33% branchlets) were gathered from a tree 4 cm in diameter, near at the time of falling leaves.

Sample V : The material was collected at Zatō-Dani (250 m alt.) in Nishinomiya-shi, Hyogo Prefecture, on November 4, 1973. The shoots (consisting of 49% leaves, 43% branchlets, and 8% flower buds) were gathered from a large tree 20 cm in diameter.

6) Y. Fujita, M. Kikuchi, and S. Fujita, *Yakugaku Zasshi*, **95**, 162, 235, 241 (1975).

Table II. Compositions of the Various Essential Oils of the Sample (V) Collected at Zatō-Dani, Hyogo Pref.

Peak No.	Component	Sample V_A Leaves	Sample V_B Branchlets	Sample V_C Flower buds	Sample V_D Flowers
1	α-Pinene	—	0.6	0.7	0.2
2	Camphene	—	0.2	0.1	0.1
3	β-Pinene	0.1	1.8	2.0	0.7
4	Limonene	0.4	0.5	0.8	0.6
5	1,8-Cineole	0.2	**23.8**	0.5	0.5
6	*p*-Cymene	trace	1.8	0.2	0.3
7	*cis*-Alloocimene	trace	1.4	1.9	0.6
8	Unidentified	trace	0.2	trace	0.1
9	*trans*-Linalool oxide	—	0.2	0.1	0.1
10	Fenchone	—	0.3	0.5	0.5
11	*cis*-Linalool oxide	—	0.2	0.1	0.1
12	Linalool	trace	1.2	1.4	1.6
13	Camphor	—	0.5	0.9	0.6
14	Terpinen-4-ol	0.1	3.5	1.3	1.4
15	Caryophyllene	trace	0.4	3.0	2.7
16	Methylchavicol	**91.4**	7.0	10.0	8.5
17	α-Terpineol	0.1	1.0	2.0	1.5
18	Citral-b	1.0	**19.7**	**22.6**	**24.2**
19	Citral-a	1.9	**30.2**	**38.1**	**43.3**
20	Nerol	—	1.1	0.1	0.1
21	Geraniol	0.1	2.0	0.2	0.1
22	*trans*-Anethole	2.9	1.0	5.6	3.5
23	Safrole	0.5	—	2.5	2.3
24	Methyleugenol	0.1	0.1	2.0	2.7
25	*p*-Anisaldehyde	0.2	0.1	—	—
26	Eugenol	—	0.8	3.0	3.5
27	Unidentified	—	—	—	—

A: Leaves of sample V.
B: Branchlets (~1 cm in diameter) of sample V.
C: Flower buds (average length 24×8 mm; its weight, 0.53 g) of sample V.
D: The flowers (average weight of one flower, 2.2 g; consisting of 80% petals and 20% carpels) were gathered from the same tree, on April 6, 1973.

Isolation of Essential Oils——Each of the fresh materials cut in small pieces was subjected to steam distillation on the 2nd or 3rd day after gathering. The distilled oil was extracted with $(C_2H_5)_2O$, and the extract was dried over anhydrous Na_2SO_4. The essential oil was obtained after evaporation of $(C_2H_5)_2O$. The weight of fresh materials used, oils obtained, and physical properties of each oil are shown in Table III.

Table III. Properties of the Materials and the Essential Oils obtained

Sample	I	II	III	IV	V_A	V_B	V_C	V_D
Part distilled	shoots (leaves and branchlets)				leaves	branchlets	flower buds	flowers
Weight of fresh materials (g)	2600	170	2300	1600	1720	1520	295	119
Weight of the oil obtained (g)	20.5	1.8	18.0	14.5	24.5	7.8	11.2	1.1
Yield (%)	0.79	1.06	0.78	0.92	1.42	0.51	3.80	0.92
d_4^{30}	0.9207	0.9466	0.9419	0.9303	0.9248	0.9000	0.8795	—
n_D^{30}	1.5082	1.5146	1.5095	1.5016	1.5178	1.4802	1.4874	0.4912
	(28)	(28)	(28)	(28)	(20)	(20)	(20)	—
$a^{(1)}_D$ (°)	-1.25	-1.85	-0.45	-1.10	+0.15	-3.85	-3.30	—
A.V.	0.6	1.3	4.2	2.1	—	—	—	—
E.V.	2.5	8.6	20.5	6.5	—	—	—	—

Analysis of Oils——Each component of the essential oils was identified mainly by the comparison of retention time in gas-liquid chromatography using columns of PEG 6000 (30%) and Silicone DC-550 (30%) with that of the oils from the methylchavicol, safrole, and methyleugenol type *M. salicifolia*, and also the anethole type *M. salicifolia*.