Notes

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

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Since 1966, a careful comparison of the essential oils of *Magnolia salicifolia* Maxim. (Japanese name, "Tamushiba") gathered from various localities in Japan, was performed from the view-point of chemical systematics and chemical taxonomy.

In a previous paper,[2] we reported the composition of the essential oils of shoots, trunk, and flowers collected at Mt. Ōhira, and its neighborhood, Kawanishi-shi, Hyogo Prefecture. These plants may be classified as the methylchavicol, safrole, and methyleugenol type.

We report now the results of the examination of the essential oils of the anethole type. This is the typical form of this species.

The essential oils were obtained in 0.56—0.89% yields by steam distillation of the fresh leaves and branchlets. The chemical compositions are shown in Table I.

Table I. Compositions of the Essential Oils of the Anethole Type *M. salicifolia* (%)

Peak No.[a]	Component	Sample I_A	Sample II	Sample III	Sample IV	Sample I_B
		Shoots (leaves and branchlets)				Trunks
		Nagano Pref.	Kyoto Pref.	Nara Pref.	Okayama Pref.	Nagano Pref.
1	α-pinene	0.6	0.1	0.2	0.2	0.2
2	camphene	0.2	0.1	0.1	—	—
3	β-pinene	2.7	0.1	0.6	0.4	0.2
4	limonene	4.8	2.3	3.0	2.0	—
5	1,8-cineole	6.9	1.2	4.2	3.8	**34.0**
6	*p*-cymene	0.4	0.2	0.3	0.4	1.0
7	*cis*-alloocimene	0.6	0.3	0.6	0.5	1.0
8	unidentified	0.1	0.1	—	—	—
9	*trans*-linalooloxide	0.1	0.1	0.1	0.1	0.2
10	fenchone	0.1	0.1	0.1	0.1	0.1
11	*cis*-linalooloxide	0.1	0.1	0.1	0.1	0.2
12	linalool	0.3	0.2	0.3	0.2	0.8
13	unidentified	—	0.1	0.1	0.2	0.2
14	camphor	0.2	0.2	0.2	0.2	2.0
15	terpinen-4-ol	1.0	0.5	1.0	0.6	5.4
16	caryophyllene	0.7	0.4	0.3	0.7	1.7
17	methylchavicol	0.5	4.0	4.5	4.8	—
18	α-terpineol	0.2	2.0	2.9	1.6	0.2

1) This forms "Miscellaneous Contributions to the Essential Oils of the Plants from Various Territories. XXXIV." Part XXXIII: S. Fujita and Y. Fujita, *Yakugaku Zasshi*, **39**, 1679 (1973).
2) Part I: S. Fujita and Y. Fujita, *Chem. Pharm. Bull.* (Tokyo), **20**, 2251 (1972). 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*; *b*) *Midorigaoka, Ikeda-shi, Osaka.*

Peak No.[a]	Component	Sample I_A Shoots (leaves and branchlets) Nagano Pref.	Sample II Kyoto Pref.	Sample III Nara Pref.	Sample IV Okayama Pref.	Sample I_B Trunks Nagano Pref.
19	citral-b	7.0	6.3	4.9	6.6	**20.2**
20	citral-a	8.3	11.0	9.0	11.4	**27.6**
21	nerol	0.1	0.2	0.2	0.1	1.1
22	*cis*-anethole	0.2	0.4	0.2	0.1	—
23	geraniol	0.1	0.1	0.1	0.1	1.6
24	*trans*-anethole	**63.4**	**64.8**	**64.0**	**64.1**	1.7
25	safrole	0.1	1.0	0.2	0.4	—
26	methyleugenol	—	0.4	—	0.1	—
27	anisaldehyde	0.6	2.4	0.9	0.5	—
28	eugenol	0.1	0.2	0.4	0.1	—
29	unidentified	0.4	0.8	0.8	0.5	—

a) GLC: PEG6000 (30%), 160°, 80 ml/min H_2

The characteristic of these oils is the abundant existence of *trans*-anethole (63.4—64.8%). But the trunk afforded the oil in 0.12% yield and the characteristic components were 1,8-cineole (34.0%), citral-b (20.2%), and citral-a (27.6%) as same as that of the methylchavicol, safrole, and methyleugenol type.

The essential oil of the plant of this type gathered from Saeki-district, Hiroshima Prefecture was examined already by Matsuura, *et al.*[4] and the oil from leaves and branchlets was shown to contain anethole (73%), 1,8-cineole (1%), citral (a small amount), anisaldehyde (7%), and other unidentified compounds.

Experimental

Materials——Sample I: On August 28, 1967, the material was collected at the foot of Mt. Ena (about 750 m above the sea level) in Nagano Prefecture.

A: The shoots (the average length of a twig: 48 cm; its weight: 7 g, consisted of 57% leaves and 43% branchlets) were gathered from three trees of 3—3.5 cmϕ.

B: The trunks (2—2.5 cmϕ) were gathered from the above trees.

Sample II: On September 2, 1967, the material was gathered at Kibune in Kyoto city (about 540 m above the sea level). The shoots (the average length of a twig: 42 cm; its weight: 6.5 g, consisted of 62% leaves and 38% branchlets) were gathered from a germinated small tree.

Sample III: On August 18, 1967, the material was gathered at the foot of Mt. Misen, in Nara Prefecture (about 600 m above the sea level). The shoots (the average length of a twig: 50 cm: its weight: 19 g, con-

Table II. Properties of the Materials and the Essential Oils Obtained

Sample	I_A	II	III	IV	I_B
The part distilled	shoots (leaves and branchlets)				trunks
Weight of fresh materials (g)	3000	36	700	175	1000
Weight of the oil obtained (g)	22.5	0.2	6.2	1.2	1.2
Yield (%)	0.75	0.56	0.89	0.69	0.12
d_4^{30}	0.9281	—	0.9681	0.9429	—
n_D^{30}	1.5178	1.5342	1.5254	1.5262	1.4786
$\alpha_D^{22}(^\circ)$	−2.75	—	−0.60	−1.85	—
A.V.	0.4	—	0.6	0.8	7.2
E.V.	11.7	—	22.0	19.6	15.2

4) T. Matsuura and Y. Watanabe, *J. Sci. Hiroshima Univ.*, **A**, **16**, No. 1, 169 (1952).

sisted of 63% leaves and 37% branchlets) were gathered from a tree 8 cmϕ.

Sample IV: On October 23, 1967, the material was gathered at Niimi-shi, in Okayama Prefecture (about 600 m above the sea level), the tree was near to the stage of leaf falling. The shoots (the average length of a twig: 25 cm; its weight 6 g, consisted of 67% leaves and 33% branchlets) were gathered from a tree 3 cmϕ.

Isolation of the Essential Oils——The each fresh material cut in small pieces was subjected to steam distillation at the 2nd or 3rd day after gathering. The distilled oil was extracted with ether, and then dried over anhydrous sodium sulfate. After distillation of the ether, the essential oil was obtained.

The weight of fresh materials used, the oils obtained, the yields of oil to the fresh materials, and the physical properties of each oil were shown in Table II.

Analysis of the Oils——The each component of essential oil was identified by the comparison of retention time of gas-liquid chromatography, with that of authentic samples and the oil of methylchavicol, safrole, and methyleugenol type *M. salicifolia*,[2] together with IR spectra of the eluted fractions of column chromatography using activated alumina (300 mesh).

trans-Anethole: Peak 24 (Table I) (IR cm^{-1}: 2960, 2930, 2840, 1605, 1575, 1510, 1470, 1440, 1375, 1305, 1285, 1250, 1175, 1160, 1110, 1035, 965, 840, and 790) was isolated, and determined as *trans*-1-propenyl-4-methoxybenzene by a comparison of the IR spectrum with that of an authentic sample.

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Organometallic Compounds. XVI.[1] Synthesis of *trans*-1,2-Diferrocenoylethylene

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trans-1,2-Dibenzoylethylene has been synthesized by the Friedel–Crafts reaction of benzene and fumaric chloride.[3] Whereas, the reaction of ferrocene and fumaric chloride in the presence of aluminum chloride catalyst did not gave expected *trans*-1,2-diferrocenoylethylene (I) but saturated compound, 1,2-diferrocenoylethane (III) and β-ferrocenoylpropionic acid (IV) were isolated, which was reported by Sugiyama and Teitei.[4]

trans-1,2-Dibenzoylethylene has also been synthesized by the condensation of ω-bromoacetophenone with alkaline[5] or dehydrogenation of 1,2-dibenzoylethane with selenium dioxide.[6] Therefore, these methods were applied for the corresponding ferrocene derivatives, but I could not be obtained.

However, the Friedel–Crafts reaction of ferrocene and fumaric chloride in presence of large excess amount of sodium chloride using 10—30 times for aluminum chloride catalyst in methylene chloride was carried out carefully protecting from moisture during the reaction. *trans*-1,2-Diferrocenoylethylene (I), mp 220° (decomp.) and *trans*-β-ferrocenoylacrylic acid (II), mp 170—171°, were isolated together with III from the reaction mixture in 18.5% and 5% yield, respectively. The infrared (IR) spectrum of I showed at 1620 cm^{-1} of carbonyl group which shifted ($\Delta\nu$ −45 cm^{-1}) over the ketone (III), and equivalent ethylene protons appeared at δ 7.52 in their nuclear magnetic resonance (NMR) spectrum. The structure

1) Part XV: K. Yamakawa, R. Sakaguchi, and K. Osumi, *Chem. Pharm. Bull.* 22, 576 (1947).
2) Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo, 162, Japan.*
3) R.E. Lutz, *Org. Syntheses, Collective Vol.* **III**, 248.
4) N. Sugiyama and T. Teitei, *Bull. Chem. Soc. Japan*, **35**, 1423 (1962).
5) K.F. Armstrong and R. Robinson, *J. Chem. Soc.*, **1934**, 1650.
6) J.P. Schaefer, *J. Am. Chem. Soc.*, **84**, 713 (1962).