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Sesquiterpene Constituents of the Essential Oil of Mitsuba (*Cryptotaenia japonica* Hassk)

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The chemical constituents of the essential oil of Mitsuba, *Cryptotaenia japonica* Hassk, were investigated by Hirao[1] quite a long time ago; he isolated a sesquiterpene hydrocarbon which produced eudalene on sulfur dehydrogenation and suggested the name "mitsubaene" for it. However, the structure of this component has not yet been established.

As is shown in Fig. 1, a sesquiterpene portion of the essential oil showed eleven peaks on gas chromatography using Diasolid L-Carbowax 6000 (3%). These components, after being isolated upon fractional distillation, preparative gas chromatography, and/or elution chromatography, were characterized by various spectrometries and by gas-chromatographic comparisons with authentic specimens.

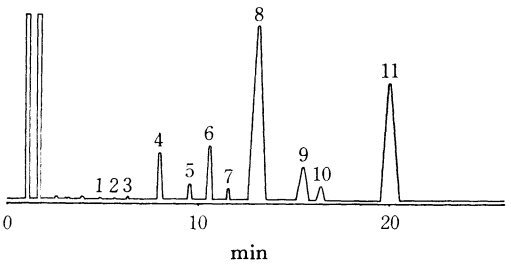

Fig. 1. Gas chromatogram of mitsuba oil (I) at 110°C on Diasolid L-Carbowax 6000.

(+)-α- and (+)-β-Selinenes. The component of the largest peak, 8, isolated by preparative gas chromatography is represented by the molecular formula of $C_{15}H_{24}$ (M^+, *m/e* 204); it was hydrogenated over Adams catalyst in acetic acid to produce a saturated hydrocarbon, $C_{15}H_{28}$ (M^+, *m/e* 208). This evidence indicates the component to be a bicyclic sesquiterpene. The IR spectrum, however, suggested that the component was a mixture of α- and β-selinenes[2]; the further separation into two components was accomplished by eluting it, step by step, over silver nitrate (10%)-coating silica gel with mixed solvents of benzene and *n*-hexane. One component, M^+ *m/e* 204, n_D^{25} 1.5040, $[\alpha]_D^{15}$ +6.31°, which was eluted more easily with a benzene and *n*-hexane-mixed solvent (v/v 10 : 90), exhibited IR and NMR spectra superimposable on those of α-selinene.[3,4] The other, M^+ *m/e* 204, n_D^{25} 1.5013, $[\alpha]_D^{15}$ +43.56°, which was eluted with a benzene and *n*-hexane mixture (v/v 15 : 85), exhibited IR and NMR spectra which were in good agreement with those of β-selinene.[5] Accordingly, the main constituents of the essential oil are (+)-α- and (+)-β-selinenes.

β- and (−)-γ-Elemenes. Both components from the 4 and 5 peaks possess the same molecular formula of $C_{15}H_{24}$ (M^+, *m/e* 204), and each uptook three molar equivalents of hydrogen on catalytic hydrogenation over Adams catalyst in acetic acid to give saturated compounds of $C_{15}H_{30}$ (M^+, *m/e* 210), whose IR spectra both coincided with that of hexahydroelemene.[3] The IR spectra of these components, however, were different from each other in the relative intensity of the absorption bands at 907 and 888 cm^{-1}; the IR spectrum of the component corresponding to the 4 peak was superimposable on that of β-elemene,[3] while that of the 5 peak on that of γ-elemene.[6] This result also agreed with those obtained by NMR and mass spectrometry and/or a gas-chromatographic comparison using an authentic specimen.[7] Although the γ-elemene isolated from this essential oil showed the following constants: n_D^{20} 1.5016, $[\alpha]_D^{20}$ −3.9°, there is some doubt whether these elemenes are natural products or artifacts, for the essential oil was collected by steam distillation. The physical constants of β-elemene were not taken.

α-Ylangene, α- and β-Copaenes, Eremophilene, Cuparene, δ-Elemene and α-Cubebene. In addition to the above components, five

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2) The authors wish to thank Professor Shô Itô of Tohoku University for kindly providing the IR and NMR spectra of a mixture of of α- and β-selinenes.

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Table 1. Sesquiterpene components of *Cryptotaenia japonica*

Peak No.	Component	Content (%)	Means of identification
1	unidentified	0.2	
	δ-elemene		GLC
	α-cubebene		GLC
2	α-ylangene	0.3	IR,[3] NMR,[9] mass,[10] GLC
	α-copaene		IR,[11] NMR,[12] mass, GLC
3	β-copaene	0.5	IR,[13] GLC
4	β-elemene	7.5	IR,[3] NMR,[14,15] mass,[10] GLC
5	(−)-γ-elemene	3.4	IR,[6] NMR, mass, GLC
6	unidentified	8.9	
7	unidentified	2.5	
8	(+)-β-selinene	20.2	IR,[5] NMR,[5] mass
	(+)-α-selinene	18.6	IR,[3] NMR,[4] mass
9	eremophilene	9.1	IR,[16] NMR,[17] mass
10	unidentified	4.6	
11	cuparene	24.2	IR,[18] NMR,[15] mass[18]

components, α-ylangene, α- and β-copaenes, eremophilene, and cuparene, were isolated; they were identified by the methods listed in Table 1. Furthermore, two components of δ-elemene and α-cubebene were tentatively assigned by comparison with the authentic specimens obtained by gas chromatography using Gas Chrom P-Apiezon L.

The relative composition of the sesquiterpene components in the essential oil of mitsuba was calculated to be as shown in Table 1 from the peak areas on the gas chromatogram measured by the use of Carbowax 6000 at 110°C. Hirao's mitsubaene, which was separated by fractional distillation only, seems to be a mixture of these components. This conclusion does not contradict the fact that he obtained eudalene by the sulfur dehydrogenation of mitsubaene.

Experimental

The gas chromatograms were taken with a Shimadzu GC-2B apparatus equipped with a hydrogen-flame ionization detector by using two separation columns (4 mm×3 m), packed with Diasolid L-Carbowax 6000 (3%) and with Gas Chrom P-Apiezon L (4.6%). Preparative gas chromatography was carried out with Celite-Carbowax 6000 (20%) (8 mm×3 m). The NMR spectra were taken in a $CDCl_3$ solution, using tetramethylsilane as the internal standard.

Fractional Distillation of the Essential Oil of Mitsuba. As has been reported in a previous paper on the monoterpene constituents,[8] the essential oil obtained by the steam distillation of the whole herb of Mitsuba was fractionated into thirty-four fractions using a spining-band distillation column under reduced pressure. The fractions (Fr. 1—11), bp 82—140°C/50 mmHg, totaled 26.46 g; they corresponded to the monoterpene constituents used for the previous investigation. The present work was carried out on Fr. 12—34, bp 84.5—168.0°C/3 mmHg, 40.30 g. These fractions were further separated into individual components by means of preparative gas chromatography or elution chromatography over silica gel impregnated with silver nitrate.

NMR of γ-elemene: One tert-methyl (1.05 ppm, 3H, s), three allylic methyls (1.67, 6H, s and 1.71, 3H, d, J=1.2 Hz), and five olefin protons (4.63—5.20, 4H, m and 5.81, 1H, q, J=18 and 10 Hz).

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