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The Volatile Constituents of Some Plants of the Compositae Family

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Full analyses of the essential oils obtained from Yomena (*Aster indicus* L.), Yomogi (*Artemisia princepts* Pamp.) and Hog weed (*Ambrosia elatior* L.) were carried out. Each essential oil was separated by fractional distillation under reduced pressure, and the fractions thus obtained were identified.

The so-called Yomena and Yomogi (the *Aster indicus* L. and *Artemisia princepts* Pamp. respectively) are the most common plants of the Compositae family which grow wild all over in Japan. Hog weed (*Ambrosia elatior* L.), which was derived from North America at the beginning of the Meiji era, has been naturalized and is widely distributed in this country now.

Some studies have been reported on the essential oils obtained from these plants. Uchida¹⁾, for instance, analyzed the oil derived from all ground parts of the Yomena obtained in the northeastern district of China and found dipentene, bornyl formate, bornyl acetate, a monoterpene alcohol with a myrtenol-like odor, a sesquiterpene hydrocarbon, and a monocyclic tertiary sesquiterpene alcohol. Nakao and Shibue²⁾ isolated cineol and α-thujone from the volatile oil derived from Japanese Yomogi grass, and Sörensen³⁾ identified a polyacetylene compound called dehydromatricaria ester in the same plant of foreign origin.

This paper will present full analyses of the essential oils obtained from these three plants of the Compositae family, Yomena, Yomogi, and hog weed.

Method

The analyses of these oils were carried out as follows. Each essential oil was subjected to fractional distillation under reduced pressure with a Podbielniaks 13 mm. Heli-Grid column, and the fractions thus obtained were analyzed by gas chromatography (GLC) and infrared spectroscopy (IR). Further fractionations by means of column chromatography on silicic acid were applied to the fractions which seemed to be complicated. Moreover, for the final estimation these methods were supplemented with ultraviolet spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry (MS).

Gas Chromatography.—Gas chromatography was carried out using a Shimadzu GC-2C-type gas chromatograph with polyethylene glycol (30%) on celite and a Hitachi F-6 gas chromatograph with a capillary column (HB-2000). In both of these cases, nitrogen was adopted as the carrier gas.

Liquid Chromatography. — Mallinchrodt's silicic acid was used as the adsorbent, and a hexane solution of ether (3%, 5%, 10%, 30%), as the elute solvent.

Mass Spectrometry.—The mass spectrometry was measured by means of a Hitachi mass spectrometer, RMU 6-type, under the following conditions: ionization voltage, 80 V.; ion source temperature, 250°C, ion accelerative voltage, 2 kV.; inlet vapor temperature, 150°C.

Experimental and Results

Yomena Oil.—Eighty-seven kilograms of the leaves and above-ground parts of the grass gathered at the beginning of October was steam-distilled; 34 cc. of the essential oil was thus obtained. This oil was subjected to fractional distillation and divided into seven fractions. The distillation residue was then steam-distilled to recover the higher boiling components.

The results are summarized in Table I.

TABLE I. FRACTIONS OF THE YOMENA OIL

Fraction No.	Volume ml.	Calcd. b. p. °C/760 mmHg
1	2	170—223
2	2	223—247
3	2	247—251
4	2	251—266
5	2	266—267
6	2	267—268
7	3.5	268—271
Steam-distd. fraction	2.5	—
Residue	15.0	—

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1) S. Uchida, *J. Soc. Chem. Ind., Japan* (*Kōgyo Kwagaku Zasshi*), **29**, 124 (1926).

2) M. Nakao and C. Shibue, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **1924**, 639.

3) K. Stavholt and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 1567 (1950).

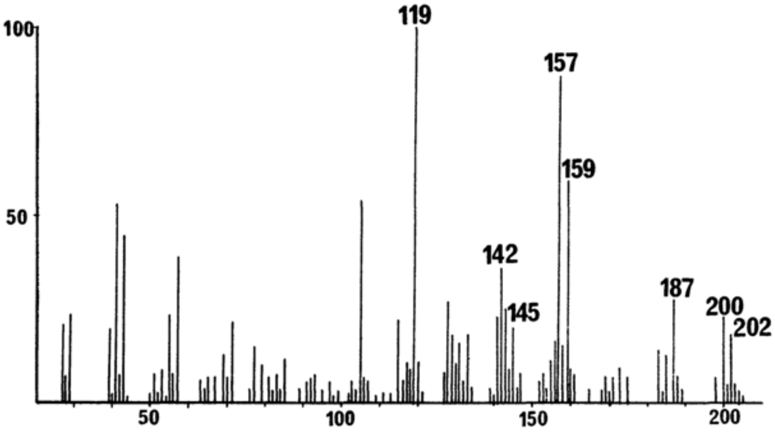


Fig. 1. The mass spectrum of calamenene fraction.

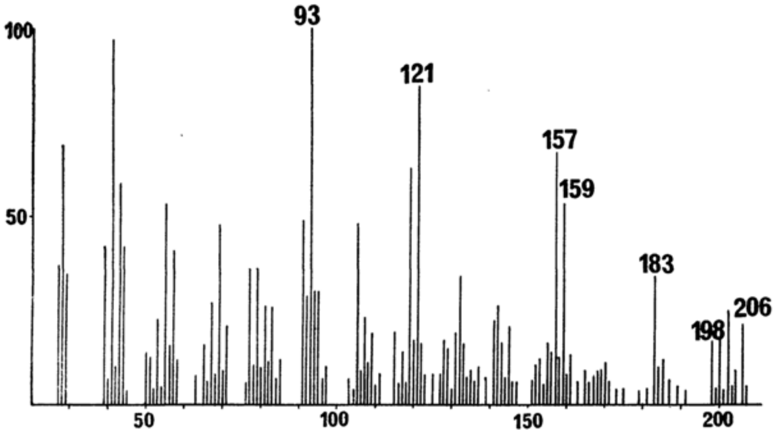


Fig. 2. The mass spectrum of calamenene and calacorene fraction.

Fraction 1 contained *p*-cymene, limonene, bornyl acetate, citronellyl acetate, phenylethyl acetate, borneol and terpineol. A hydrocarbon which was very similar to myrcene in its IR spectrum but not in its GLC was isolated from this fraction. Its spectroscopic character (IR: 6.1, 6.2, 9.02, 10.1, 11.2, 13.2 μ. UV: $\lambda_{max}^{\text{Ethanol}}$ 234.9 mμ) indicates the presence of conjugated dienes, at least one of which has an end methylenic feature. This is further supported by the fact that the hydrocarbon suffers oxidation and polymerization rather soon after being exposed to the atmosphere. These characteristics suggest that the hydrocarbon is likely to be ocimene.

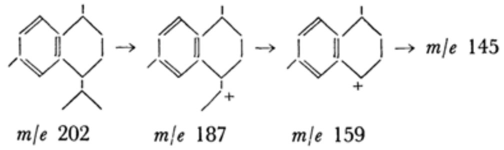
Fractions 2 to 4 were found to contain β-elemene as the main constituent, together with small amounts of bornyl acetate, benzyl alcohol, camphor, borneol and phenylethyl alcohol.

Fractions 5 to 7 and the volatile part recovered from the distillation residue were composed solely of sesquiterpene hydrocarbons. From these fractions, β-elemene, caryophyllene, humulene, α-curcumene, calamenene, δ-cadinene and γ-cadinene were identified by means of IR and GLC measurements. In addition to these compounds, a hydrocarbon corresponding to β-selinene in GLC was isolated. Its MS spectrum was also very similar to that of β-selinene. However, the IR and MS spectra of β-selinene has no remarkable characteristics to distinguish them from others, and further attempts to identify it definitely were discontinued because of the limited amount of material available.

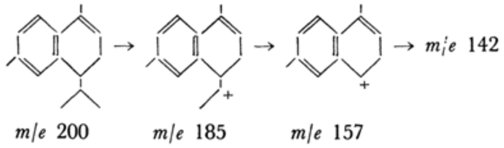
The volatiles recovered from the distillation residue contained humulene, caryophyllene, γ- and δ-cadinene, calamenene and a sesquiterpene hydrocarbon whose IR spectrum was very similar to β-cadinene. The calamenene separated by the chromatography of this fraction was shown to include calacorene by IR, GLC and MS spectrum studies. The MS spectrum of calamenene fraction is shown in Fig. 1.

The peaks at *m/e* 187, 159, 145 and 202 are derived by the fragmentation of calamenene (MW. 202), while the peaks at *m/e* 200, 185, 157 and 142 are derived by the fragmentation of calacorene (MW.

200). These fragments can be illustrated as follows:



Calamenene



Calacorene

The compounds identified from Yomena oil are listed in Table II.

TABLE II. COMPOUNDS IDENTIFIED FROM YOMENA OIL

Compound	Content, %
p-Cymene	0.4
Ocimene ?	0.9
Limonene	0.3
Aromatic hydrocarbon	0.3
Borneol	0.3
Camphor	0.3
Bornyl acetate	6.1
Citronellyl acetate	+
Terpinyl acetate	+
Phenylethyl acetate	+
Terpineol	+
Phenylethyl alcohol	+
Benzyl alcohol	0.3
β-Elemene	22.8
Caryophyllene	2.9
Humulene	4.9
γ-Cadinene	3.4
δ-Cadinene	0.7
β-Cadinene	+
α-Curcumene	1.3
Calamenene	4.2
Calacorene	2.8

Yomogi Oil.—Yomogi oil (160 cc.) obtained by the steam distillation of 58 kg. of the grass dried in the shade was submitted to fractional distillation under diminished pressure and then divided into 16 fractions. A mixture of borneol and camphor (15 g.) was removed from the pot material by filtration in the course of distillation, because the crystallization of those compounds at the take-off arm of the distillation column obstructs further operation; the distillation was then carried on again. The distillation residue was steam-distilled to recover the volatiles (Fraction 17).

The results are summarized in Table III.

TABLE III. FRACTION OF THE YOMOGI OIL

Fraction No.	Volume ml.	Calcd. b. p. °C/760 mmHg
1	5	165—184
2	5	184
3	5	184
4	10	184—208
5	10	208—211
6	1	211—213
7	5	213—235
8	5	235—268
9	5	268—269
10	6	269
11	4	269—276
12	2	276—281
13	2	281—285
14	4	285—287
15	2	287—288
16	4	288—290
17	4	—
Residue	71	—

Fractions 1 to 3 consisted of α-pinene, camphene, myrcene, *p*-cymene and cineol, which was the principal constituent of these fractions.

γ-Terpinene, cineol, artemisia ketone, matsutakeol and α-thujone were separated from Fraction 4 by column chromatography. Artemisia ketone was identified by comparing its IR, MS spectra and GLC results with those of an authentic sample[*1] obtained from the volatile oil of *Artemisia annua* L.

Fractions 5 to 7 contained bornyl acetate, camphor, piperitone and borneol. A sesquiterpene hydrocarbon which was separated by the chromatography of Fraction 7 displayed major absorption peaks in the IR spectrum at 11.1 and 14.3 μ and gave predominant peaks in its MS spectrum at *m/e* 189, 175, 161 and 119 (base peak) indicating that it might be a patchoulene-type compound.

Fraction 8 contained ylangene, caryophyllene, β-elemene, creosol, borneol and an aromatic acid. Fractions 9 and 10 consisted mainly of caryophyllene. As Fractions 8 to 10 were shown to contain some carbonyl compounds by a study of their IR spectra, a mixture of these fractions was treated by a Girard T reagent in the usual manner; the small amounts of carbonyl compounds were separated which were shown by GLC to contain at least three compounds. One of them was identified as α-ionone by means of IR, MS spectra and GLC.

Fractions 11 to 16 contained β-elemene, caryophyllene, humulene, curcumene, γ-cadinene, δ-cadinene and a sesquiterpene keotne, which gave a 2, 4-dinitrophenyl hydrazone (m. p. 167—173°C). The chromatographic fraction containing calamenene and calacorene separated from Fraction 17 was shown by its MS spectrum to include two additional hydrocarbons.

[*1] The authors wish to thank Professor Tsunematsu Takemoto for providing us with an authentic sample of artemisia ketone.

The two series of peaks at *m/e* 202 and 159 and at *m/e* 200 and 157 are derived by the fragmentation of calamenene and calacorene respectively. The peaks at *m/e* 206, 121 and 93 show the existence and the fragmentation of a perhydro-sesquiterpene hydrocarbon whose molecular weight is 206. The peaks at *m/e* 198 and 183 are derived from a dehydrogenated sesquiterpene hydrocarbon, which is likely to be a naphthalene compound, such as cadalene or eudalene, with a molecular weight of 198.

The results of the analysis of Yomogi oil are shown in Table IV.

TABLE IV. THE CONSTITUENTS OF YOMOGI OIL

Compound	Content, %
α-Pinene	0.6
Camphene	1.6
Myrcene	1.5
p-Cymene	0.2
γ-Terpinene	2.2
Cineol	3.2
Artemisia ketone	2.5
Matsutakeol	2.7
α-Thujone	1.0
Bornyl acetate	2.5
Camphor	10.5
Piperitone	0.5
Borneol	15.4
α-Ionone	+
Creosol	0.2
Ylangene	1.0
Caryophyllene	2.9
β-Elemene	+
Humulene	4.1
γ, δ-Cadinene	2.6
β-Cadinene	0.5
α-Curcumene	5.2
Calamenene	1.6
Calacorene	0.5
β-Selinene ?	0.1
Hydrocarbon (MW 206)	+
Hydrocarbon (MW 198)	+
Sesquiterpene hydrocarbon	0.1
Sesquiterpene ketone	0.9

Hog Weed Oil.—Upon the steam distillation of the hog weed grass (60 kg.) collected in the middle of October, 19 cc. of volatile oil was obtained. The oil was subjected to fractional distillation and was divided into four fractions (Table V). Each fraction was treated in the way described above.

TABLE V. FRACTION OF HOG WEED GRASS OIL

Fraction No.	Volume ml.	Calcd. b. p. °C/760 mmHg
1	2.9	155—190
2	2	190—252
3	2	252—273
4	0.7	273—300

Fraction 1 consisted solely of monoterpene hydrocarbons; the gas chromatogram of this fraction showed that these hydrocarbons were α-pinene, camphene, β-pinene, myrcene and limonene.

Fractions 2 to 4 consisted of rather complicated sesquiterpene hydrocarbons and contained at least nine compounds. The chromatographic analyses of those fractions showed the presence of ylangene, δ-cadinene, γ-cadinene and curcumene. As to the other compounds, however, no further characterization could be attained owing to the small quantities of them available and difficulties in separating them from each other.

The composition of hog weed oil is shown in Table VI.

TABLE VI. COMPOSITION OF THE VOLATILE FRACTION OF HOG WEED GRASS

Compound	Content, %
α-Pinene	4.7
Camphene	0.1
β-Pinene	0.5
Myrcene	0.5
Limonene	9.8
Ylangene	0.5
δ-Cadinene	2.5
γ-Cadinene	2.0
α-Curcumene	5.0
Unidentified five hydrocarbons	24.3

Summary

Volatile oils obtained from three kinds of plants of the Compositae family have been analyzed.

Yomena oil contained *p*-cymene, ocimene, limonene, borneol, camphor, bornyl acetate, citronellyl acetate, terpinyl acetate, phenylethyl acetate, terpineol, phenylethyl alcohol, benzyl alcohol, β-elemene, caryophyllene, humulene, γ-cadinene, δ-cadinene, β-cadinene, α-curcumene, calamenene, calacorene, and an aromatic hydrocarbon.

Yomogi oil contained α-pinene, camphene, myrcene, *p*-cymene, γ-terpinene, cineol, artemisia ketone, matsutakeol, α-thujone, bornyl acetate, camphor, piperitone, borneol, α-ionone, creosol, ylangene, caryophyllene, β-elemene, humulene, γ-cadinene, δ-cadinene, β-cadinene, α-curcumene, calamenene, calacorene, β-selinene, three kinds of sesquiterpene hydrocarbon, and a sesquiterpene ketone.

Hog weed oil contained α-pinene, camphene, β-pinene, myrcene, limonene, ylangene, δ-cadinene, γ-cadinene, α-curcumene and five unidentified hydrocarbons.