エゾキスゲ花の香気成分

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Odorous Ingredients of the Flower of Ezokisuge

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南波　哲・若山　誠治*：エゾキスゲ花の香気成分

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In our series of studies on the ingredients of odorous flowers in Hokkaido, the odorous constituents of the flower oil of Ezokisuge have been examined. Lilac alcohols, benzyl cyanide and indole have been identified as the main and/or important components.

We have noticed that the flower of Ezokisuge (*Hemerocallis Yezoensis* Hara) smells agreeably on a fine day, whereas it smells rather disagreeably on a rainy day. We therefore examined the odorous ingredients of the flower oil and identified many components by gas chromatography and mass spectrometry.

Experimental

The analytical apparatus and the operating conditions : *Liquid chromatography* (LC) was accomplished on a column containing alumina, Brockmann activity grade II, manufactured by Merck.

Gas chromatography (GC) was carried out using a Hitachi Model 063 with a flame ionization detector, fitted with a 3 mm (i. d.)×2 m stainless steel column packed with 20% DEGS on 60/80 mesh Chromosorb W. The oven temperature was held isothermally at 100°C for 10 min, then programmed to 190°C at 3°C/min. The carrier gas was Helium and the flow rate was 30ml/min. Two different columns, 5% SE-30 and 20% PEG 6000, were also used for comparative analysis.

Combined gas chromatography and mass spectrometry (GC/MS) : A Hitachi RM 50-GC combined with Model 063 equipped with a DEGS column. Ionization voltage : 70 eV, Ionsource temperature : 220°C, Detector : Total ion monitor.

Materials and methods. Ezokisuge flowers were collected at Nishikioka, Tomakomai, during June to July when in full bloom, and were extracted with n-hexane to yield a concrete (0.11% of the flower), which on steam distillation gave a pale yellow oil in a 1.7×10^{-5}% yield of the flower.

The oil was fractionated into five portions by means of LC, using n-hexane (H), n-hexane-benzene (1 : 1 v/v) (H-B), benzene (B), ether (E) and methanol (M), successively. The reflux of the alumina with methanol containing 2% HCl consequently afforded a mixture of acid methyl esters (M-HCl). Each eluate was analyzed and identified by a comparison of their chromatographic retention times and their mass spectra, being always checked against those of respective authentic specimens.

The non volatile residue was digested with methanol and was divided into methanol-insoluble wax (53%) and methanol-soluble fraction (47%). After treatment of the methanol-soluble fraction with sodium carbonate, acidic (76%) and acid-free (24%) fractions were obtained. The wax and the acid-free fraction were subjected to separation by LC, and were analyzed by GC and GC/MS. The acidic components were converted to their methyl esters and then identified by GC and GC/MS.

Results and Discussion

A gas chromatogram of the flower oil of Ezokisuge is shown in Fig. 1. Table 1 lists the identities of the peaks, where for some peaks the formulae or mass numbers of molecular ions (M^+) by the deduction of their mass spectra are given, together with the fraction in LC.

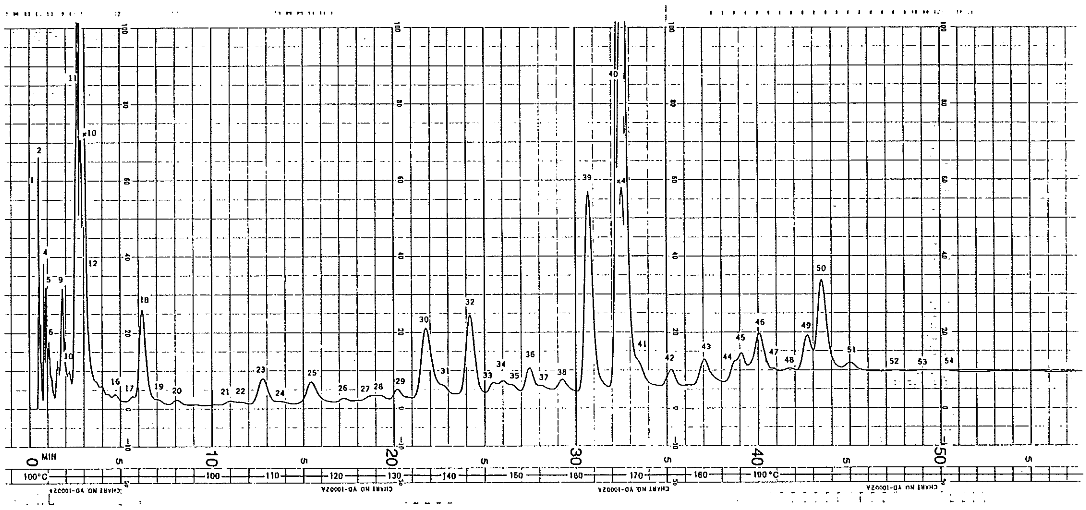

Fig. 1 Gas Chromatogram of Flower Oil of Ezokisuge.
(Hemerocallis Yezoensis Hara)

A 3mm (i. d.)×2m stainless steel column packed with 20% DEGS on 60/80 mesh Chromosorb W, the oven temperature was held at 100℃ for 10min then programmed to 190℃ at 3℃/min, carrier gas flow rate, He, 30ml/min.

Table 1

Peak No.	Compound	Source (LC fraction)
1-5	Unidentified (ui.)	
6	α-Pinene	H
7, 8	ui.	H, H-B
9	β-Pinene	H
10	$M^+=136$, $C_{10}H_{16}$ ui.	H
11	$M^+=136$, $C_{10}H_{16}$ ui.	H
12	ui.	E
13, 14	ui.	H-B, B
15	ui.	B, E
16	ui.	H, B
17	ui.	H-B
18	$M^+=188$, ui.	H-B
19	ui.	B
20	n-$C_{15}H_{32}$	H
21	trans-Linalool oxide (THF)	B
22	cis-Linalool oxide (THF)	B
23	Linalool	B
24	Camphor	H-B
25	Benzaldehyde	H-B
26	ui.	B
27	n-$C_{17}H_{36}$	H
28	ui.	B
29	ui.	H
30	Lilac alcohol b	E
31	Lilac alcocol d	E
32	Lilac alcohol a	E
33	p-Dimethoxybenzene	H-B
34	Lilac alcohol c	E
35	n-$C_{19}H_{40}$	H
36	Phenethyl ester ui.	H-B
37	ui.	B
38	Benzyl alcohol	E
39	β-Phenethyl alcohol	E
40	Benzyl cyanide	H-B
41	n-$C_{21}H_{44}$	H
42	γ-Phenylpropyl alcohol	E

43	Anisaldehyde &	B
	Cinnamaldehyde	E
44	ui.	H-B
45	n-$C_{23}H_{48}$	H
46, 47	ui.	H-B
48	ui.	B
49	Elemicine	B
50	Cinnamyl alcohol	E
51	n-$C_{25}H_{52}$	H
52, 53	ui.	B
54	Indole	H-B
55-62	ui.	

The characteristic MS patterns of several important components are described in the following tables.

Benzyl cyanide : MS, m/e ; 117 (M^+, 100), 116 (34), 89 (19), 77 (7), 63 (8), 51 (11), 39 (8).

Indole : MS, m/e ; 117 (M^+, 100), 90 (38), 89 (22), 63 (9), 58.5 (9).

Lilac alcohol a : MS, m/e ; 170 (M^+, 1.7), 155 (10.3), 111 (71.6), 93 (58.7), 55 (100), 43 (83), 41 (55.3), 31 (24.2).

Lilac alcohol b : MS, m/e ; 170 (M^+, 1.5), 155 (10.8), 111 (72.3), 93 (57.7), 55 (100), 43 (86.2), 41 (58.5), 31 (23.1).

Lilac alcohol c : MS, m/e ; 170 (M^+, 1.3), 155 (15.3), 111 (69.3), 93 (58.7), 55(100), 43 (76), 41 (56.6), 31 (21.3).

Lilac alcohol d : MS, m/e ; 170 (M^+,1.1), 155 (10), 111 (70), 93 (56), 55 (100), 43 (86), 41 (58), 31 (19).

The fraction (M-HCl) was found to contain a large number of esters. Caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic, oleic, benzoic and phenylacetic acids were identified as their methyl esters by GC and GC/MS. In the oil, those methyl esters would be present as free acids, respectively.

The non-volatile residue was composed of hydrocarbons (33%), higher aliphatic alcohols (11%), ester-bound wax (9%), acids (35%) and an acid-free methanol-soluble fraction (12%). Except for the last fraction, these components were almost entirely odourless compounds.

Hydrocarbons : All normal chain paraffins from $C_{15}H_{32}$ to $C_{33}H_{68}$ were identified. The hydrocarbons having an odd number of carbon atoms were present in significantly greater quantity than the adjucent even number of carbon atoms homologe, and C_{25}, C_{27} and C_{29} of the hydrocarbons were the dominant amounts in the mixture.

Higher alcohols : The saturated straight-chain alcohols containing an even number of carbon atoms from C_{22} to C_{32} were identified, and $C_{28}H_{57}OH$ was found to be the dominant amount in the mixture.

Wax : n-Alkyl (C_{16}–C_{32}, even) esters of fatty acids in the C_{14}–C_{24} (even) range were suggested by the results of analysis after saponification of the wax.

Acids : Pentadecanoic, heptadecanoic, arachidic, behenic, palmitoleic, linoleic and linolenic acids were identified in addition to the acids in the fraction M-HCl. Palmitic and oleic acids were the major components of these acids.

The separation of the components of the acid-free fraction was not achieved.

It is to be noted that (1) lilac alcohols[1,2], which are the most important odorous ingredients of the lilac flower, exist abundantly in *Liliaceae* as well as in *Oleaceae* and in *Rubiaceae*[3], and (2), the odor of the Ezokisuge flower is masked with benzyl cyanide and indole.

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