Components of the Essential Oil from *Matteuccia struthiopteris*

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Abstract: A steam distilled oil obtained from *Matteuccia struthiopteris* was analyzed by GC and GC/MS. The oil was found to contain 103 volatile components, and (*E*)-phytol (24.8%), nonanal (15.1%) and decanal (7.6%) as the main compounds. The oil included two aldehydes known as sea-weed like odor, (8*Z*, 11*Z*, 14*Z*)-heptadecatrienal (0.6%) and (8*Z*, 11*Z*)-heptadecadienal (0.1%). The most characteristic aroma compound was (6*Z*)-nonenal.

Key words: *Matteuccia struthiopteris*, Dryopteridaceae, essential oil, (*E*)-phytol, (8*Z*, 11*Z*, 14*Z*)-heptadecatrienal, (8*Z*, 11*Z*)-heptadecadienal, (6*Z*)-nonenal

1 INTRODUCTION

Matteuccia struthiopteris ('Kusasotetsu' in Japanese) is a fern of the Dryopteridaceae and an edible wild plant that grows in colonies at damp area. It has been called 'Kogomi' and eaten as fry or tempura principally in the northeast part of Japan. Also the young buds can pick in April-June are eaten as boiling seasoned with soy sauce. Lately it comes to be cultivated for mass production.

It is known to have strong faculty for eliminating active oxygen and as the radical scavenger, chlorogenic acid¹⁾ and *L*-*O*-caffeoylhomoserine²⁾ from *M. struthiopteris* were reported. Moreover legumin- and vicilin-like proteins have been isolated from spores of the fern³⁾. Also dolichols have been isolated from leaves of the fern⁴⁾. Thus it comes to be a remarkable plant recently.

However, no studies on the essential oil from *M. struthiopteris* have been reported. The aim of this paper is therefore to identify the essential oil content and detect the important odor-active compounds from *M. struthiopteris*.

2 EXPERIMENTAL

2.1 Material plant

Samples of *M. struthiopteris* were harvested from Fukushima prefecture in Japan in April 2006.

2.2 Isolation of the essential oil

The above ground parts of *M. struthiopteris* (500 g) was hydrodistilled using a Likens-Nickerson-type apparatus with diethyl ether as the solvent to yield 0.002% of oil, which was dried over anhydrous sodium sulphate prior to analyses.

2.3 Gas chromatography (GC)

GC was carried out using a Hewlett Packard 6890 chromatograph equipped with a flame ionization detector (FID) on a capillary column (DB-WAX 15 m × 0.25 mm, film thickness 0.25 μm). The column temperature was programmed from 40°-260°C at a rate of 4°C/min and held at 260°C for 5 min. The injector and detector temperatures were 270°C and 280°C, respectively. The flow rate of the carrier gas (He) was 1.4 mL/min. Split ratio was 1:10.

2.4 Gas chromatography/mass spectrometry (GC/MS)

GC/MS was carried out with a Hewlett-Packard 6890/Hewlett-Packard 5973 instrument. GC conditions were equipped on two capillary columns (DB-WAX 15 m × 0.25 mm, film thickness 0.25 μm; HP-5MS 30 m × 0.25 mm, film thickness 0.25 μm). On DB-WAX, the GC oven temperature was kept at 40°C for 5 min and programmed to 260°C at a rate of 4°C/min and then kept constant at 260°C for 5 min. On HP-5MS, the column temperature was programmed from 40°-260°C at a rate of 4°C/min and held at 260°C for 5

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min. The injector and detector temperatures were 270°C and 280°C, respectively. The flow rate of the carrier gas (He) was 1.4 mL/min. The detector interface temperature was set at 280°C with the actual temperature in the MS source reaching approximately 230°C and the ionization voltage 70 eV. Split ratio was 1:10. Acquisition mass range was 39-450 amu.

2.5 Gas chromatography/mass spectrometry-olfactometry (GC/MS-O)

GC/MS-O was carried out using a Hewlett Packard 6890/Hewlett Packard 5973-Olfactory Detection Port 2. GC condition was equipped on a capillary column (HP-5MS 30 m × 0.25 mm, film thickness 0.25 µm). The column temperature was programmed from 40°-260°C at a rate of 4°C/min and held at 260°C for 5 min. The injector and detector temperatures were 270°C and 280°C, respectively. The flow rate of the carrier gas (He) was 1.4 mL/min. The detector interface temperature was set at 280°C with the actual temperature in the MS source reaching approximately 230°C and the ionization voltage 70 eV. Split ratio was 1:10. Acquisition mass range was 39-450 amu. The Chemstation software acquired two channel signals simultaneously, one channel for MS, and other channel from the olfactometer signal board. A signal sniffer, the author, recorded the aroma character manually.

2.6 Aroma extract dilution analysis (AEDA)

The flavor dilution (FD)-factor of the odorants in the essential oil was determined by aroma extract dilution analysis (AEDA) of the following dilution series⁵⁾. The highest dilution was defined as FD-factor 1 (6.9 mg/ml). The oil was stepwise diluted (1+1, v/v) by addition of

diethyl ether. Aliquots were then analyzed by GC/MS-O on the capillary column HP-5MS. The highest dilution at which an individual component could be detected was defined as the FD-factor for that odorant.

2.7 Identification of constituents

The components of the oil were identified by direct comparison with authentic samples on the basis of retention time and GC/MS, confirmed by analyses of authentic samples from the published in the literature⁶⁾ and our previous papers⁷⁻¹²⁾.

3 RESULT AND DISCUSSION

The yield of oil obtained by steam distillation from *M. struthiopteris* was 0.002% (w/w). Total ion chromatogram (TIC) of this oil showed the presence of 103 compounds (Fig. 1). As far as could be ascertained, 76 compounds (93.8% of the total oil) were identified for the first time in this study on the oil from *M. struthiopteris* (Table 1). The main components were (*E*)-phytol (24.8%), nonanal (15.1%) and decanal (7.6%). The oil was determined to be rich in many chain aldehydes.

Two unsaturated long-chain aldehydes were detected in the oil and identified as (8*Z*,11*Z*)-heptadecadienal (0.1%) and (8*Z*,11*Z*,14*Z*)-heptadecatrienal (0.6%) (Fig. 2). They are odor compounds of green alga, such as *Ulva pertusa*¹³⁾, *Monostroma nitidum*¹⁴⁾ and *Enteromorpha prolifera*¹⁵⁾, and known as representative seaweed aroma. The aldehydes have been isolated from not only seaweed but terrestrial plants, such as tobacco leaves¹⁶⁾, wheat¹²⁾ and honey-suckle flowers¹⁷⁾.

Fig. 1 The Total Ion Chromatogram of Essential Oil from *Matteuccia struthiopteris*.

DB-WAX (15 m × 0.25 mm i.d., film thickness 0.25 µm); flow rate of the carrier gas (He), 1.4 mL/min; oven temperature, 40°-260°C at 4°C/min and held at 260°C for 5 min.

Table 1 Compounds of the Essential Oil from *Matteuccia struthiopteris*.

No	RI-W ^{a)}	RI-5 ^{b)}	Compound	Percentag	No	RI-W	RI-5	Compound	Percentag
1	800	800	octane	tr.	50	1786		nerol	0.3
2	900	900	nonane	tr.	51	1793		2-tridecanone	0.2
3	1049		hexanal	0.3	52	1799	1511	tridecanal	0.3
4	1161	902	heptanal	12.6	55	1828		α -ionone	0.1
5	1195		1-pentanol	0.9	56	1836		geraniol	0.2
6	1212	990	2-pentyl-furan	0.2	58	1889		phenylethyl alcohol	0.2
7	1235	985	3-octanone	0.5	59	1909	1613	tetradecanal	0.8
10	1270	1001	octanal	1.7	60	1917	1489	β -ionone	0.6
11	1282		1-octen-3-one	0.2	62	1953		caryophyllene oxide	tr.
12	1310		2-methyl-3-octanone	0.3	64	2011	1716	pentadecanal	6.1
14	1345	866	haxanol	1.8	66	2058		3-methyleicosane	tr.
15	1380	1105	nonanal	32.6	69	2100	2100	heneicosane	0.2
16	1389	993	3-octanol	3.6	70	2111	1847	6,10,14-trimethyl 2-pentadecanone	0.2
17	1400	1400	tetradecane	tr.	71	2117	1817	hexadecanal	0.3
18	1416	1096	(6Z)-nonenal	tr.	73	2161	1315	4-vinyl- <i>o</i> -guaiaicol	0.7
21	1444	977	1-octen-3-ol	10.0	74	2200	2200	docosane	0.3
22	1450	968	heptanol	tr.	75	2201		methyl palmitate	0.1
23	1457		<i>trans</i> -linalool oxide	0.3	76	2221	1919	heptadecanal	0.1
24	1471		α -copaene	tr.	78	2261		heptadecanol	0.3
25	1476	1382	protoillud-6-ene	0.6	79	2277		isophytol	tr.
26	1485	1207	decanal	16.3	80	2300	2300	tricosane	2.6
27	1492	958	benzaldehyde	7.0	82	2358	1895	(8Z,11Z,14Z)-heptadecatrienal	0.6
28	1515		(2E)-nonenal	0.8	83	2365		octadecanol	0.3
29	1540	1101	linalool	8.0	84	2400	2400	tetracosane	tr.
30	1550	1068	octanol	0.9	85	2408	1295	indole	0.2
31	1567	1433	γ -elemene	0.5	87	2500	2500	pentacosane	0.7
33	1579		terpinen-4-ol	0.2	90	2548	1889	(8Z,11Z)-heptadecadienal	0.1
34	1585		2-undecanone	0.2	91	2563		(Z)-phytol	0.2
36	1595		β -cyclocitral	0.4	93	2610	2117	(E)-phytol	24.8
37	1606		(2E)-nonenol	1.0	94	2662		phenanthrene	tr.
38	1612	1043	phenylacetaldehyde	3.3	95	2700	2700	heptacosane	0.4
40	1652	1160	nonanol	1.4	97	2800		octacosane	0.1
41	1667	1164	4'-hydroxy-acetophenone	0.9	99	2900		nonacosane	0.2
42	1672		(3Z)-nonenol	0.7	100	2929		hexadecanoic acid	0.7
43	1681		α -terpineol	0.7	101	3000		triacontane	0.2
44	1693	1410	dodecanal	1.7	102	3058		squalene	0.1
45	1701	1184	naphthalene	1.0	103	3100		hentriacontane	0.1
46	1714		1,2-dihydro-1,1,6-trimethyl-naphthalene	0.2					
47	1753		decanol	0.4				total	93.8

^{a)}RI-W: Retention index on a DB-WAX column; ^{b)}RI-5: Retention index on a HP-5MS column; Percentage was rdetected to total detected compounds by GC; tr: trace<0.1%.

Table 2 Odor-active Compounds in the Essential Oil from *Matteuccia struthiopteris*.

^{a)} RI-5	FD-factor	Aroma quality	Aroma compound
873	16	green odor	hexanol
897	8	bitter odor	heptanal
919	1	fatty odor	unknown
973	4	sweet, mushroom-like odor	1-octen-3-ol
997	2	refreshing odor	octanal
1040	16	green, earthy odor	phenylacetaldehyde
1076	16	plastic-like odor	unknown
1090	64	green, refreshing odor	(6Z)-nonenal
1096	8	fresh, floral odor	linalool
1176	32	earthy odor	unknown
1192	2	green, refreshing odor	nonanal
1382	2	vegetable-like odor	unknown
1304	1	green, vegetable-like odor	unknown

^{a)} RI-5: Retention index on a HP-5MS column.

Fig. 2 Structure of Two Unsaturated Long-chain Compounds from *Matteuccia struthiopteris*.

Thereupon the important odor-active compounds in essential oil from *M. struthiopteris* were analyzed by GC/MS-O and AEDA to estimate that the characteristic aldehydes were concerned with odor of *M. struthiopteris*. The results of GC/MS-O and AEDA studies were given in Table 2. Two unique aldehydes couldn't be smelt because of the low concentration. (6Z)-Nonenal savors green like odor played an important role in the characteristic aroma of *M. struthiopteris* (FD-factor>64). Besides green like odor, linalool as sweet odor concerned with aroma of the oil.

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