Comparison of the Essential Oils of *Glehnia littoralis* from Northern and Southern Japan

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The essential oils from aerial and root parts of *Glehnia littoralis* were investigated by GC and GC−MS, and 125 compounds were identified. Plants were obtained from Northern and Southern Japan, and samples from the same locations were cultivated either exposed or unexposed to sunlight. The main constituents of the essential oils were found to be α-pinene (0.03−13.40%), limonene (0.15−10.71%), *β*-phellandrene (0.03−22.93%), germacrene B (0.27−8.33%), spathulenol (0.24−6.50%), *β*-oplopenone (0.06−6.47%), panaxynol (0.38−24.58%), propyl octanoate (3.44−27.85%), hexadecanoic acid (0.45−27.80%), and linoleic acid (0.16−17.56%). Terpenoid compounds were found in higher concentrations in the Northern type oils than in the Southern types, whereas the concentration of polyacetylenic compounds was higher in one of the Southern samples, except from the aerial parts of those cultivated exposed. Consequently, the constitution of the essential oils from *G. littoralis* could be separated into Northern and Southern types.

Keywords: *Glehnia littoralis; essential oil; blanching culture; panaxynol*

INTRODUCTION

Glehnia littoralis Schmidt ex Miquel (Japanese name: Hamaboufu) is a perennial herb of the family Umbelliferae growing wild on the sandy shores in Japan and was classified into Northern and Southern types (N and S type) on the basis of HPLC profiles of eight furanocoumarins and a polyacetylenic compound, panaxynol, in the underground parts (*1*). The N type plants, growing in the northern part of the country, contained more than 0.1% of furanocoumarins such as imperatorin, isoimperatorin, and 8-geranyloxypsoralen, whereas the S type plants, distributing in the southern part, contained less than 0.1% of these components. The ratio of the panaxynol content to the total content of eight furanocoumarins was 0−2 in the N type plants vs 10−100 in S type plants. The boundary regions of the distribution of the two types were found to be the Noto Peninsula on the Sea of Japan coast and the Sanriku Coast on the Pacific Ocean side (*1*−*3*). *Glehnia* root (*Glehniae* Radix cum Rhizome) is listed in the Japanese and Chinese Pharmacopoeia and has been used as a diaphoretic, an antipyretic, and an analgesic in the traditional medicine of these countries. Aerial parts are used for salads and as an aromatic vegetable. Hatta et al. (*4*, *5*) reported that the germination rates, seed weight, root yield, and extract yield of the cultivated plants of *G. littoralis* varied depending upon the place of growth of the plants. Our present findings demonstrate that in this plant species, the chemical components also vary considerably depending upon the plant origin. The variation could be caused by genetic, environmental, and physiological factors. The subterranean parts of *G. littoralis* are affected by factors such as the duration of growth, moisture content of soil, atmospheric temperature, or concentrations of macronutrients. Since about 1870, *G. littoralis* has been grown under blanching culture, protected from sunlight under sand and a roof, which is believed to give roots that are softer and delicious. Therefore, the composition under blanching and unblanching culture was compared. However, no comparison of the essential oils from two origins (N and S types) of *G. littoralis* has been reported. The present investigations were aimed at identifying and comparing the essential oils in plant material obtained from Northern and Southern Japan, but grown in the same location.

MATERIALS AND METHODS

Plant Material. Plants were cultivated in the herb garden at Niigata College of Pharmacy, Niigata, Japan.

G. littoralis came from Niigata (Northern type) and Chiba (Southern type) prefecture. Blanching cultures were protected from sunlight under sand and a roof. Plants were planted April 5, 1998 and were harvested May 15, 1998. All of the samples were immediately dried at 60 °C for 63 h.

Samples could be classified into eight groups: (A) = N type, unblanching culture, aerial part; (B) = N type, unblanching culture, root part; (C) = N type, blanching culture, aerial part; (D) = N type, blanching culture, root part; (E) = S type, unblanching culture, aerial part; (F) = S type, unblanching culture, root part; (G) = S type, blanching culture, aerial part; (H) = S type, blanching culture, root part.

Extraction of Essential Oil. Air-dried samples were obtained by hydrodistillation for 2 h using a Likens−Nickerson-type apparatus, and using diethyl ether as solvent to yield a yellowish oil, which was dried over anhydrous sodium sulfate.

The yields of oils were as follows: (A) 0.10%; (B) 0.09%; (C) 0.11%; (D) 0.09%; (E) 0.20%; (F) 0.17%; (G) 0.16%; and (H) 0.10%.

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Table 1. Components of the Essential Oils of *G. littoralis* (%)

			sample[a]							
no.	compound[b]	RI[c]	A	B	C	D	E	F	G	H
1	α-pinene	1020	0.24	13.40	0.11	5.68	0.56	0.05	0.03	tr[d]
2	camphene	1064		1.74		0.78				
3	hexanal	1080	0.08	0.08	0.04	0.17		0.16	0.10	
4	*β*-pinene	1106	0.65	0.87		0.49				
5	sabinene	1114		0.29		0.08				
6	butanol	1135	0.12		0.29		tr	1.33	0.20	0.32
7	*β*-myrcene	1170	0.22	1.04	0.04	0.30				
8	α-phellandrene	1173	0.28	0.83		0.45	0.62			
9	*δ*-3-carene	1176	0.14	0.26		0.22	tr	1.38		
10	heptanal	1184	0.26	0.73	0.46	1.07	0.11	0.14	2.22	0.41
11	limonene	1198	4.90	10.71	0.15	4.87	3.17	0.18	tr	tr
12	*β*-phellandrene	1204	12.96	22.93	0.37	16.69	13.21	0.03	tr	tr
13	*p*-cymene	1265	0.42	0.77	0.06	0.76	0.18			
14	octanal	1273	0.88	2.52	2.12				4.11	3.79
15	terpinolene	1286				3.90	0.56	5.62		
16	3-methyl-2-buten-1-ol	1339	0.58	0.42	0.46	0.50	0.17	0.10	0.20	0.05
17	2-nonanone	1397		0.20	0.24	0.30		0.24	0.49	0.20
19	nonanal	1401	0.59	1.22	0.66	0.49	0.22	0.50	1.64	0.65
20	acetic acid	1441	1.74	0.33	1.32	0.92	1.71	2.19	2.48	1.77
22	tetramethyl pyrazine	1473	2.42		5.03	0.92	0.45		2.02	2.65
24	propyl octanoate	1508	16.89	5.41	9.25	3.44	20.81	26.81	27.85	14.14
25	linalool	1550	0.43	0.22	1.08	0.23	0.16	tr	0.08	0.03
26	octanol	1556	0.15	0.53	0.26	0.80	0.62			0.41
27	*cis-p*-menth-2-en-1-ol	1562	0.36	0.16	0.07	0.30	0.21	0.70		
28	*β*-cedrene	1573	0.12		0.07	0.08	0.18		0.07	0.09
29	bornyl acetate	1581	0.12	1.11	0.13	0.43	0.39	0.26		0.10
30	*β*-elemene	1591	0.22	1.73	0.92	1.78	0.64	0.18		
31	*trans-β*-caryophyllene	1598		0.21	0.41	0.47	1.20			
32	terpinen-4-ol	1605	0.08	0.40	0.73	0.39	1.20			0.10
34	*γ*-elemene	1628	0.53	4.07	0.70	6.95	3.50	0.10	tr	tr
35	3-decanol	1632	tr		0.13	tr		0.22	0.04	2.34
36	benzeneacetaldehyde	1656	0.24	0.21	0.22	0.53	0.21	0.10	0.36	0.90
38	*β*-farnesene	1664	0.49	0.09	0.11		0.30	0.75		
39	α-gurjunene	1693	1.15	0.29	0.18	0.32				
40	acoradiene	1698	tr	0.57	0.73	1.31	0.30		0.07	1.79
41	α-terpineol	1681	0.27	0.17	0.31	0.31	0.14	0.59		
42	germacrene D	1693	tr	0.36		0.39	0.24	0.62		
43	*β*-selinene	1715	0.27	0.40	0.73	1.34	0.41		0.17	0.22
45	α-selinene	1725	0.07	0.29	0.44		0.11			
47	*δ*-cadinene	1745	0.36	0.61	0.99	3.05	0.31	tr	0.04	0.20
50	*β*-guaiene	1748		0.29	0.20	0.43				0.05
51	selin-4,7(11)-diene	1750		0.46	0.51	0.69	0.14			
52	*trans,trans*-2,4-decadienal	1751		0.40						0.61
53	ar-curcumene	1784	0.15		0.66	0.59	0.32		0.13	0.51
55	α-elemene	1799	0.18	1.12	1.41	1.97	0.58			0.14
56	cuparene	1803	0.08	0.38	0.37	0.89			0.04	0.58
57	germacrene B	1824	tr	6.68	0.73	8.33	3.82	tr	0.27	tr
63	geraniol	1828	0.24		0.62	0.82			0.04	
64	*p*-cymen-8-ol	1850	0.08	0.09	0.07	0.31				0.10
67	neophytadiene	1961	1.13	tr	0.31	0.07	1.60	0.11	0.06	tr
69	heptanoic acid	1950			0.21	0.36			0.08	0.34
70	hexanoic acid	1861		0.13						0.88
71	caryophyllene oxide	1983	0.30	tr	0.12	0.14	0.40	0.32	0.04	0.20
72	methyl eugenol	2015	0.09		0.33	0.13				3.19
73	carotol	2033	2.08	0.10	1.77	0.33	0.43	2.66	0.15	0.07
75	octanoic acid	2062	0.22	0.40	0.46	0.51	0.14	0.10	0.22	0.12
77	*β*-eudesmol	2120	0.27	tr	0.90	1.08	0.15	2.06	0.10	0.37
78	2-metoxy-4-vinyl-phenol	2146	0.12	0.17	0.11	0.32		0.08		0.60
79	*γ*-decalactone	2160			0.24				0.28	0.71
80	nonanoic acid	2165	0.23	0.17	0.22	0.39	0.13	0.36	tr	3.50
81	decanoic acid	2260	0.62	0.21	0.90	0.32	0.33	0.30	0.04	0.44
83	2-propyl hexadecanoate	2310	0.42	1.47	1.66	2.73	0.51	0.42	0.14	
84	spathulenol	2338	0.49	3.06	6.50	4.14	1.08	1.42	0.24	0.46
92	dodecanoic acid	2489	0.42	tr	0.20	0.12	0.46	0.43	0.13	0.56
93	*β*-oplopenone	2496	0.20	tr	6.47	3.14	0.91	0.42	0.06	0.12
95	vulgarone B	2508	0.32	1.70	4.29	2.08	0.79	0.59	0.32	0.34
96	ethyl linolate	2520	0.12		0.04	0.03	0.40		0.04	0.40
97	2-hexadecen-1-ol	2574						0.11	0.46	0.24
98	nonadecanal	2604	0.20		0.05	0.03	0.33	0.30	0.14	0.31
100	phytol	2622	4.21	tr	tr	tr	7.39	0.10	0.46	0.25
101	tetradecanoic acid	2717	1.44	0.23	0.06	0.27	0.79	2.71	2.11	1.28
102	heptacosane	2700		0.08			0.24	tr	0.29	0.95
103	pentadecanoic acid	2820	0.99	0.26	0.26	0.16	0.24	0.83	3.84	2.67
116	hexadecanoic acid	3041	14.45	0.48	15.67	0.45	5.16	4.29	17.80	6.16
117	heptadecanoic acid	3067	0.31	0.05	0.13	0.08	0.10	tr	1.50	1.84
119	panaxynol	3086		0.38	1.32	0.81	9.23	24.53	1.75	24.58
120	octadecanoic acid	3130	0.39				0.10	0.37	0.42	0.65
121	oleic acid	3150	0.69	0.33	tr	tr	0.16	0.37	1.20	0.87
124	linoleic acid	3215	8.79	0.46	17.56	0.16	2.68	4.17	14.15	5.27
125	linolenic acid	3250	5.47	tr	1.48	0.09	2.11	0.80	1.57	0.36

[a] A = North, unblanching, aerial; B = North, unblanching, root; C = North, blanching, aerial; D = North, blanching, root; E = South, unblanching, aerial; F = South, unblanching, root; G = South, blanching, aerial; H = South, blanching, root. [b] All components were identified by comparing retention times of GC and GC/MS with those of authentic samples. [c] Retention induces (RI) on TC-WAX. [d] tr = trace (<0.01%).

Table 2. Classification of Eight *G. littoralis* Samples on the Basis of Essential Oil Composition

	sample							
compound	A	B	C	D	E	F	G	H
aliphatic	90.43	93.43	83.04	83.66	91.55	89.71	87.92	80.61
hydrocarbons	24.17	69.40	8.84	52.85	31.88	9.02	1.09	3.25
(monoterpenoid)	19.81	52.84	0.73	28.22	18.30	7.26	0.03	tr[a]
(sesquiterpenoid)	3.15	16.56	7.80	24.56	11.74	1.65	0.71	2.80
(diterpenoid)	1.13		0.31	0.07	1.60	0.11	0.06	tr
alcohols	9.36	5.15	13.19	9.21	11.55	9.31	1.97	4.74
(monoterpenoid)	1.46	1.04	2.88	2.36	1.71	1.29	0.12	0.23
(sesquiterpenoid)	2.84	3.16	9.17	5.55	1.66	6.16	0.49	0.90
(diterpenoid)	4.21		tr	tr	7.39	0.10	0.46	0.25
aldehydes & ketones	2.89	7.46	9.32	10.33	2.67	2.35	9.12	6.69
(monoterpenoid)	0.36	0.61	0.99	3.05	0.31	tr	0.04	0.20
(sesquiterpenoid)	0.52	1.70	4.76	5.22	1.70	1.01	0.38	0.46
acids	30.99	3.05	37.78	3.74	12.00	16.12	44.39	26.35
esters	23.02	7.99	12.56	6.72	24.22	28.29	29.60	15.00
polyacetylene	tr	0.38	1.32	0.81	9.23	24.53	1.75	24.58
aromatic	2.95	0.76	6.06	2.79	0.66	0.18	2.42	7.92
hydrocarbons	0.08	0.38	0.37	0.89			0.04	0.58
phenolics	0.12	0.17	0.11	0.32		0.08		0.60
heterocyclics	2.42		5.03	0.92	0.45		2.02	2.65
miscellaneous	0.33	0.21	0.55	0.66	0.21	0.10	0.36	4.09
miscellaneous	6.62	5.81	10.90	13.55	7.79	10.11	9.66	11.47

[a] tr = trace (<0.01%).

Gas Chromatography (GC). GC was carried out using a Hewlett-Packard 5890 instrument equipped with a flame ionization detector on a capillary column (TC-WAX FFS fused silica 60 m × 0.25 mm i.d.) from GL science. The column temperature was programmed from 80 °C to 250 °C at the rate of 4 °C/min and held at 250 °C for 47 min. The injector and detector temperatures were 250 and 280 °C, respectively. Flow rate of the carrier gas (He) was 1.0 mL/min.

Gas Chromatography−Mass Spectrometry (GC−MS). MS was carried out with a Hewlett-Packard 5972 mass selective detector. GC conditions were the same as previously described. The detector interface temperature was set at 280 °C, with the actual temperature in the MS source reaching approximately 180 °C, and the ionization voltage was 70 eV.

Identification of Components. The components of these oils were identified by comparison of their mass spectra with those of a computer library or with authentic compounds, and they were confirmed by comparison of their retention indices with either those of authentic compounds or with data published in the literature (*6*) and by our previous work (*7*−*10*).

RESULTS AND DISCUSSION

The essential oils collected by steam distillation from the eight samples of *G. littoralis* were obtained in yields of 0.09−0.20% (w/w). Distinct qualitative and quantitative differences were observed in the eight oils studied. Gas chromatograms of these oils showed the presence of 125 compounds (Table 1), which amounted to 88.40−94.19% of the total components detected. The main components of the essential oils from *G. littoralis* samples were α-pinene (0.03−13.40%), limonene (0.15−10.71%), *β*-phellandrene (0.03−22.93%), propyl octanoate (3.44−27.85%), *γ*-elemene (0.10−6.95%), germacrene B (0.27−8.33%), hexadecanoic acid (0.45−17.80%), panaxynol (0.38−24.58%), and linoleic acid (0.16−17.56%).

Northern Type. The main components of unblanching-grown aerial parts were aliphatic hydrocarbons, acids, and esters. Unblanching-grown root parts had aliphatic hydrocarbons, which accounted for about 70% of the essential oil. Blanching culture decreased aliphatic hydrocarbon monoterpenoids and increased aliphatic hydrocarbon sesquiterpenoids relative to unblanching culture.

Southern Type. Unblanching-culture aerial parts contained aliphatic hydrocarbons, acids, and esters. Unblanching-culture roots had aliphatic acids, esters, and polyacetylenes. It is noticeable that polyacetylenes were identified as major components, whereas in the Northern type they were minor components. Blanching culture decreased aliphatic hydrocarbons and increased acids relative to unblanching culture. Polyacetylene amounts did not fluctuate.

The classification of samples on the basis of structure type is summarized in Table 2.

Samples (A) and (E) are similar on the basis of essential oil composition. Sample (B) is characterized by a high content of aliphatic hydrocarbons and low content of acids, esters, and polyacetylene, whereas (F) possessed a lower aliphatic hydrocarbons level and higher acids, esters, and polyacetylene levels. We previously reported that *G. littoralis* root extracted with ether contained eight furanocoumarins and polyacetylenes, which permitted classification into N and S types. The essential oil of *G. littoralis* supported the distinction between N and S types, which contained different essential oil components. In particular, polyacetylene content is in agreement with the data obtained in previous studies (*1*, *11*, *12*). It is of interest that N and S type plants grown in same field had different amounts of constituents. We believe that each type has noticeable differences in the quantities of physiologically active secondary metabolites which could be caused by genetic factors, and *G. littoralis* from different sources should affect the qualities of the crude drug derived therefrom.

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