Distribution of Terpenes and Phenol Ethers of *Asarum* Species Growing in Islands in Pacific Ocean

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A survey of chemical compositions of ten species of *Asarum* subgenus *Heterotropa* growing in some islands in Pacific Ocean showed that two groups could be distinguished on the basis of terpene and phenyl propane compositions.

Introduction

The genus *Asarum* of the Aristolochiaceae with 70 species has a wide distribution in Asia, Europe, and North America. The Asiatic species of the genus were placed by Maekawa [1] in the three genera, *Heterotropa* (ca. 40 species), *Asarum* (one species), and *Asiasarum* (three species). There are some islands which are called Satsunan-shoto in Pacific Ocean, as showing in Fig. 1. About ten characteristic species grow in the individual islands. In the Satsunan-shoto, the occurrence of all *Heterotropa* is limited to elevation of 280 m and more above sea level [2], indicating a relationship between their distributional pattern and the geohistory of the islands. Accordingly, it is interest to know the relationship between the geohistory of the islands and chemical compositions of *Asarum* species. From the viewpoints of morphology, Karyo-morphology, and distribution of these plants, Maekawa suggested the five species, *A. yakushimense*, *A. kumageana*, *A. yakushimense* var. *glabrum*, *A. kumageana* var. *satakeana*, *A. fudsinoi* occurring in the islands of Tokara-retto, Tanega-shima, Yaku-shima, Amami-oshima. Yuasa and Maekawa [2] examined the chromosomes of the species of *Asarum* distributed in Satsunan-shoto and found the similarity of the chromosomes of the four species, *A. celsa*, *A. gusk*, *A. hatushimae*, *A. similis*, growing in Amami-oshima and Tokuno-shima.

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In this work, the chemical compositions of ten species of *Asarum* isolated by sea were examined and then some chemosystematic aspects are discussed on the basis of terpene and phenyl propane compositions and geohistory [3] of the islands.

Experimental

The *Asarum* examined are following: *A. yakushimense* Masamune and *A. kumageana* Masamune in Yaku-shima, *A. kumageana* var. *satakeana* Maekawa in Tanega-shima, *A. yakushimense* var. *glabrum* Hatusima in Tokara-retto, *A. fudsinoi* Ito, *A. gusk* Maekawa, *A. lutchuensis* Ito, *A. celsa* Maekawa in Amami-oshima, *A. hatusimae* Maekawa and *A. similis* Maekawa in Tokuno-shima. The fresh species (50–200 g) were minced and then steam-distilled. The ether extracts of the distillates gave the essential oils which were analysed by gas chromatography (GC) and gas chromatograph-mass spectrometer (GC-MS) comparing with the spectra of the authentic specimens [4, 5].

Results and Discussion

The results show the presence of twenty monoterpenes, eighteen sesquiterpenes, six phenyl propanes, and two orcinols in the essential oils of *Asarum* as shown in Table I. Table II shows the total contents of the terpene, phenyl propane, and orcinol components. On the basis of these results the two groups could be distinguished. Group 1 contains

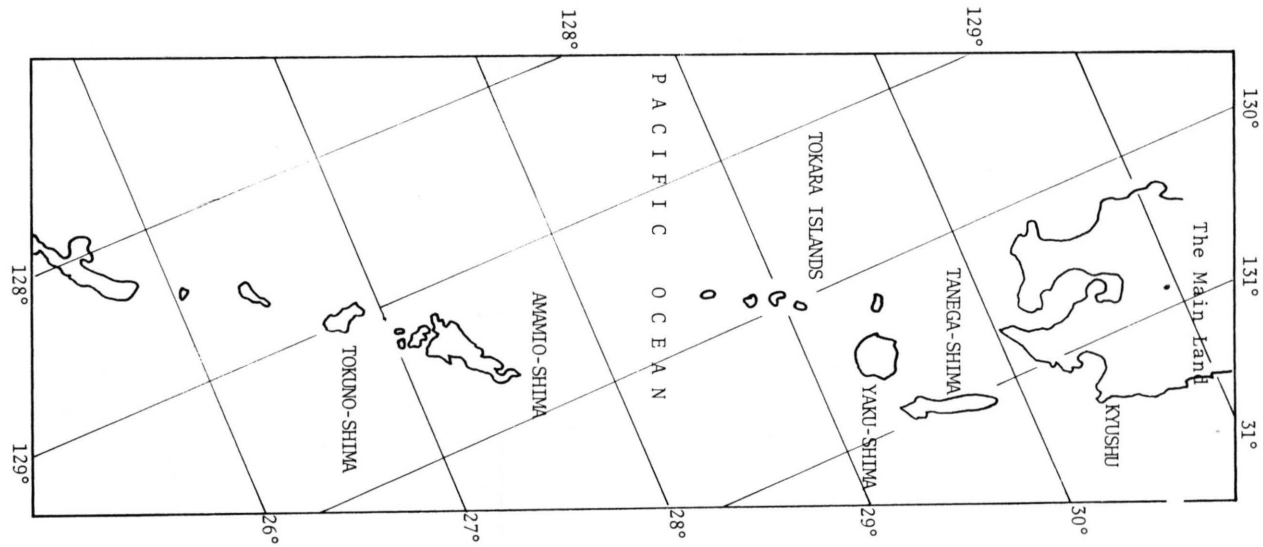


Fig. 1. Map of Satsunan-shoto in Japan.

Table I. Distribution of terpene, phenylpropane and orcinol composition of *Asarum* species.

Asarum species	*yakushimense*		*kumageana*		*kumageana* var. *satakeanum*		*yakushimense* var. *glabrum*		*lutchuensis*		*celsa*		*gusk*		*fudsinoi*		*hatushimae*		*similis*	
	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R
Monoterpene																				
α-Pinene	t	0.3	t	1.6	0.4		t	0.8		13.4	0.1	0.8					1.7	10.0	0.4	3.1
β-Pinene	t	0.2	2.1	2.1	1.3		t	3.0		16.4	0.2	12.1	0.4			0.2	1.1	17.4	0.4	10.1
Camphene			14.1	1.0	1.3		t	0.6		6.4	t	1.3					0.6	6.0	0.2	2.5
Limonene		1.0								0.7	0.4	1.9			0.7	0.5	4.1	1.1	0.7	0.8
Myrcene					1.4				7.9											
α-Phellandrene									0.7								1.6			
β-Ocimene	t								1.4								0.4			
p-Cymene											0.3	0.6	0.7	0.8	3.8	0.6	3.6		0.1	
1,8-Cineole		0.9		0.5	1.6	0.1	0.2	2.2	0.7	0.7		1.8								1.8
Linalool		0.3					1.0		1.8									1.1		
Borneol		2.6		4.5		1.8		5.9		3.9	4.4	25.4	12.2	32.1	1.1	5.7	0.3	2.3	0.5	4.5
Camphor											0.3	1.2		0.5	0.3	1.6	0.2	1.2	0.4	2.7
α-Terpineol										1.1										0.9
β-Terpineol																			2.6	
Thymol																1.0	1.0		0.1	
Thymol methylether												3.3					t	0.4		

Table I. Distribution of terpene, phenylpropane and orcinol composition of *Asarum* species.

Asarum species	*yakushimense*		*kumageana*		*kumageana* var. *satakeanum*		*yakushimense* var. *glabrum*		*lutchuensis*		*celsa*		*gusk*		*fudsinoi*		*hatushimae*		*similis*	
	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R	L	R
Linalyl acetate													0.7							
Bornyl acetate										1.3	2.1	4.5						0.8		4.1
Terpinyl acetate		0.6										1.1	0.6	2.1						
Unknown				0.6			0.1	7.5				0.9	0.5	0.6			0.9	2.8	0.6	
Sesquiterpene																				
α-Elemene					1.0		1.3													
β-Elemene							7.2		2.8		4.2								4.2	
γ-Elemene									1.6		5.0	2.3							5.0	
Copaene														4.2		2.6			0.1	
Bergamotene																	11.5			
Caryophyllene	10.9	1.5	4.8		15.6				4.2		2.8		11.9				2.9		1.5	
γ-Cadinene			2.2						7.2			5.6		14.1						
δ-Cadinene									t											3.7
α-Curcumene											6.8		1.4				25.0		23.4	0.7
α-Humulene	4.7	1.5	2.1		5.7				t											
Guaiene			22.2		1.0															
β-Cubebene											3.2									
β-Farnesene				0.5													6.8		4.2	
Bisabolene		0.4																	4.4	
Zingiberene							13.0										8.3		2.3	
α-Cedrene													3.1				4.2		1.4	
Muurolene													2.4							
Unknown	0.1	1.3	0.5			0.1			6.8		50.0	2.3	43.3	1.0		1.5	1.6	6.5		11.5
Phenylpropane																				
Eugenol													0.7			1.4				
Safrole					1.4		4.3						5.2	0.8	82.2	14.1				
Methyl eugenol	0.1	2.4	0.3	0.5	1.0	0.4	0.2	6.0	3.2	4.7	1.4		3.2	1.1	1.5	6.4		1.4	0.2	2.9
Myristicin			3.1	0.9	62.3	0.5	72.7	23.8	32.4	4.3										
Elemicin (contain isomers)	84.2	86.9	48.6	87.8	6.0	97.1		50.2	29.3	47.1	18.8	30.5	13.7	36.4	10.4	65.1	24.2	48.0	47.3	47.8
1-Allyl-2,3,4,5-tetra-methoxy benzene										t		3.2		6.3						
Orcinol																				
3,5-Dimethoxy toluene																		0.5		1.6
3,4,5-Trimethoxy toluene		0.1				t						1.2				0.1		0.5		1.3

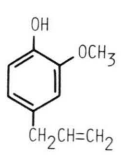
t, trace; R, roots; L, leaves.

Table II. Terpene, phenylpropane, and orcinol composition of *Asarum* species of the subgenus *Heterotropa.*

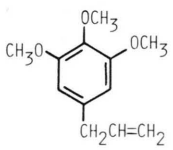
Asarum species		Terpene			Phenylpropane					Orcinol
		Mono-terpene	Sesqui-terpene	Total	Safrole	Methyl-eugenol	Myristi-cin	Elemi-cin	Total	Total
yakushimense	L	trace	15.7	15.7		0.1		84.2	84.3	
	R	5.9	4.7	10.6		2.4		86.9	89.3	0.1
kumageana	L	16.2	31.8	48.0		0.3	3.1	48.6	52.0	
	R	10.3	0.5	10.8		0.5	0.9	87.8	89.2	
kumageana var. *satakeana*	L	6.0	23.3	29.3	1.4	1.0	62.3	6.0	70.7	
	R	1.9	0.1	2.0		0.4	0.5	97.1	98.0	trace
yakushimense var. *glabrum*	L	1.3	21.5	22.8	4.3	0.2	72.7		77.2	
	R	20.0		20.0		6.0	23.8	50.2	80.0	
lutchuensis	L	12.5	22.6	35.1		3.2	32.4	29.3	64.9	
	R	43.9		43.9		4.7	4.3	47.1	56.1	
celsa	L	7.8	72.0	79.8		1.4		18.8	20.2	
	R	54.9	10.2	65.1				30.5	33.7	1.2
gusk	L	15.1	62.1	77.2	5.2	3.2		13.7	22.8	
	R	36.1	19.3	55.4	0.8	1.1		36.4	44.6	
fudsinoi	L	5.9		5.9	82.2	1.5		10.4	94.1	
	R	9.6	3.3	12.9	14.1	6.4		65.1	87.0	0.1
hatushimae	L	15.5	60.3	75.8				24.2	24.2	
	R	43.1	6.5	49.6		1.4		48.0	49.4	1.0
similis	L	6.0	46.5	52.5		0.2		47.3	47.5	
	R	30.5	15.9	46.4		2.9		47.8	50.7	2.9

L, leaves; R, roots.

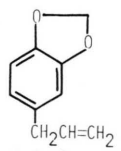
phenyl propane more than 60% of the essential oil; *A. yakushimense, A. kumageana, A. yakushimense* var. *glabrum, A. kumageana* var. *satakeana, A. lutchuense, A. fudsinoi.* Group 2 contains phenyl propane less than 60% but contains considerable amount of mono- and sesquiterpene; *A. celsa, A. gusk, A. hatushimae, A. similis.* Furthermore, the species belonging to the Group 1 contain both elemicin and myristicin in the leaves and roots except *A. yakushimense* and *A. fudsinoi,* while the species belonging to the Group 2 contain only elemicin in both leaves and roots and no myristicin. Both *A. hatushimae* and *A. similis* in the same island contain twenty percent of α-curcumene in the essential oils of the leaves and the remaining components are very similar each other. *A. hatushimae* and *A. similis* contain borneol more than twenty percent and other components are closely related.



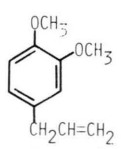
Eugenol



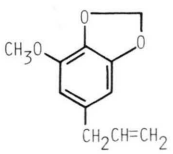
Elemicine



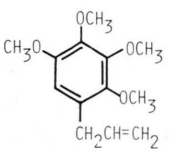
Safrole



Methyleugenol



Myristicin



1-Allyl-2,3,4,5-tetramethoxybenzene

Scheme

The species belonging to the Group 1 are distributed in the nothern part of Satsunan-shoto, while Group 2 is in southern part.

Tokara is volcanic islands which were created about one hundred thousand years old, while Tanega-shima closely related Yaku-shima was estimated to be approximately eight hundred thousand years old. On the other hand Yaku-shima and Amami-oshima were formed twenty million years old. These two islands were separated by sea approximately two million years old from the geohistory, it may be seen that the species of *Asarum* in Tokara island and Tanega-shima came from Yakushima.

Considering the content of elemicin and myristicin, the two species of Yaku-shima contain only elemicin or elemicin together with small amounts of myristicin in the leaves and roots, while the new island species distributed in Tanega-shima and Tokara islands contain the considerable amount of myristicin in the leaves together with elemicin in the roots. These results suggested that the new island species (*A. yakushimense* var. *glabrum*, *A. kumageana* var. *satakeana*) may be developed to contain high amount of myristicin in the leaves. The composition of the essential oils of *A. fudsinoi* was very different from other species in Satsunan-shoto but similar to that of *A. tukusiana* in the main land (Kyushu) of Japan.

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