Terpenic Constituents of *Asarum*

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Terpenic constituents of 23 species of subgenus *Heterotropa* growing in Japan were analyzed by means of gas chromatograph-mass spectrometer. Thirteen sesquiterpenes were identified from the essential oils together with fourteen monoterpenes. It is found that all species of *Heterotropa* contain considerable amount of mono- and sesqui-terpenes in the oils.

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Table I. Distribution of Terpenes of *Heterotropa*.

	Section *Heterotropa*	*H. asaroides*	*H. satsumensis*	*H. unzen*	*H. curvistigma*	*H. tamaensis*	*H. muramatsui*	Section *Asciasarum*	*H. aspera*	*H. hexaloba*	*H. hexaloba var. perfecta*	*H. contraversa*	Section *Bicornes*	*H. savatieri*	*H. takaoi*	*H. nipponica*	*H. nankaiensis*	Section *Sakawanae*	*H. costata*	*H. stellata*	*H. sakawana*	*H. minamitanianum*	Section *Annularia*	*H. tsukusiana*	*H. subglobosa*	*H. trigyna*	*H. kumageana*	*H. yakusimensis*
Monoterpene																											
α-pinene		+	+	+	+	+	+		+	+	+	+		+	+	+	+		+	+	+	+		+	+	+	+	+
camphene		+	+	+	+	+	+		+	+	+	+			+				+	+	+	+		+	+	+	+	+
β-pinene		+	+	+	+	+	+		+	+	+	+		+	+	+	+		+	+		+		+	+	+	+	+
myrcene					+					+					+	+	+							+	+	+	+	
α-terpinene										+																		
β-phellandrene			+		+	+	+										+											
p-cymene				+						+	+						+											
1,8-cineole				+		+	+			+	+					+	+		+		+	+		+	+	+	+	
camphor		+	+	+	+		+		+	+	+			+	+	+			+					+	+			
linalool					+	+	+			+		+		+										+		+		+
borneol		+	+	+	+	+	+		+	+	+	+		+	+	+	+		+	+	+	+		+	+	+	+	+
α-terpineol					+	+	+		+	+	+															+		
bornyl acetate					+		+				+																	
terpinyl acetate						+	+												+									
Sesquiterpene																											
α-elemene					+							+							+									
δ-elemene							+																					
copaene							+		+		+								+	+	+					+		
bergamotene		+			+				+	+									+	+	+	+		+		+	+	+
caryophyllene		+			+	+	+		+	+														+				+
α-humulene						+	+												+								+	
muurolene						+																					+	
α-cedrene			+						+										+	+	+	+				+	+	+
β-farnesene		+							+							+			+		+				+	+		
zingiberene									+											+	+	+				+		+
nerolidol									+	+											+							
elemol																					+							
farnesol																					+							

The genus *Asarum* has a wide distribution in Asia, Europe and North America. As for the Asiatic species, Morren and Decaisne [1] established the genus *Heterotropa*. More than forty species of sugenus *Heterotropa* are growing in Far Eastern Asia. *Heterotropa* is known for its characteristic ornamental and medicinal value. Some workers [2 – 4] have reported the analysis of the essential oils of *Heterotropa*. The systematic study of the essential oils was carried out by Saiki [4] by means of GLC and many phenol ether constituents were detected together with pinene and borneol. In the present study, terpenic constituents of 23 species of *Heterotropa* growing in Japan were analyzed by means of gas chromatography-mass spectrometry (GC-MS).

The taxa investigated included the following 23 species; subgenus *Heterotropa* – Section *Heterotropa*, *H. tamaensis* (Makino) F. Maekawa, *H. muramatsui* (Makino) F. Maekawa, *H. curvistigma* F. Maekawa, *H. asaroides* Morren et Decaisne, *H. satsumensis* F. Maekawa, *H. unzen* F. Maekawa. Section *Sakawanae*, *H. costata* F. Maekawa, *H. sakawana* (Makino) F. Maekawa, *H. stellata* F. Maekawa, *H. minamitanianum* (Hatusima) F. Maekawa. Section *Ascidasarum*, *H. aspera* F. Maekawa, *H. hexaloba* F. Maekawa, *H. hexaloba var. perfecta* F. Maekawa, *H. controversa* F. Maekawa nom. nud. Section *Biocornes*, *H. takaoi* F. Maekawa, *H. savatieri* F. Maekawa, *H. nipponica* F. Maekawa, *H. nankaiensis* F. Maekawa. Section *Annularia*, *H. tsukusiana* F. Maekawa, *H. subglobosa* F. Maekawa, *H. trigyna* F. Maekawa, *H. kumageana* (Masam.) F. Maekawa, *H. yakusimensis* (Masam.) F. Maekawa.

The fresh whole plant (ca. 250 g) was collected, chopped and then subjected to steam distillation. The essential oils were obtained by the extraction of the distillate with ethyl ether and by the evaporation of the solvent. The individual components of the oils were identified by means of GC-MS. Based on agreement of these spectral patterns with authen-

Table II. Terpene composition (percent) of the essential Oils of *Heterotropa*.

	Monoterpene	Sesquiterpene	Terpene Total	Phenol Ether Total	Another Component
Section *Heterotropa*					
H. asaroides	9.6	11.8	21.4	78.6	
H. satsumensis	17.2	13.1	30.3	69.7	
H. unzen	24.3	19.9	44.2	55.8	
H. curvistigma	27.1	27.9	55.0	30.6	14.4
H. tamaensis	31.5	16.5	48.0	52.0	
H. muramatsui	22.5	17.2	39.7	60.3	
Section *Ascidasarum*					
H. aspera	54.6	30.3	84.9	15.1	
H. hexaloba	18.1	7.7	25.8	74.2	
H. hexaloba var. perfecta	62.6	5.8	68.4	16.1	15.5
H. contraversa	23.8	13.2	37.0	63.0	
Section *Bicornes*					
H. savatieri	13.3	23.3	36.6	59.8	3.6
H. takaoi	6.4	17.5	23.9	70.8	6.2
H. nipponica	5.8	10.8	16.6	82.0	1.4
H. nakaiensis	28.1	6.9	35.0	57.3	7.7
Section *Sakawanae*					
H. costata	13.5	15.3	28.8	71.2	
H. stellata	23.0	59.0	82.0	18.0	
H. sakawana	25.9	68.6	94.5	5.5	
H. minamitanianum	56.0	41.1	97.1	2.9	
Section *Annularia*					
H. tsukusiana	20.7	2.3	23.0	70.8	6.2
H. subglobosa	9.8	6.3	16.1	83.9	
H. trigyna	13.1	9.3	22.4	77.6	
H. kumageana	8.1	2.1	10.2	89.8	
H. yakusimensis	0.9	37.7	38.6	61.4	

tic ones [5 – 10] identification was carried out. GC-MS was employed on a lm glass column containing 3% OV-101 on 100 – 200 mesh Chromosorb WAW. Helium was used as the carrier gas at flow rate of 15 ml/min. The column temperature was programmed from 50 to 200 °C at a rate of 5 °C/min. A total ion current detector was used to monitor the chromatographic separation of the components. All mass spectra were obtainde at 20 and 70 electron-beam voltages. Quantitation of the component was carried out by peak area measurement from GLC profiles recorded during GC-MS measurement.

The analytical results are shown in Table I and II. Table I lists the terpenes of *Heterotropa* newly identified in this study. Forteen monoterpenes (α-pinene, camphene, β-pinene, myrcene, α-terpinene, β-phellandrene, *p*-cymene, 1,8-cineole, camphor, linalool, borneol, α-terpineol, bornyl acetate, terpinyl acetate) were identified by GC-MS together with thirteen sesquiterpenes (α-elemene, δ-elemene, copaene, bergamotene, caryophyllene, α-humulene, muurolene, α-cedrene, β-farnesene, zingiberene, nerolidol, elemol, farnesol) from the essential oils. It is found that all species of *Heterotropa* contain considerable amounts of mono- and sesqui-terpenes as shown in Table II. It is interesting to note that the three species of *Sakawanae* contain large amounts of terpene up to 90%.

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